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The major part of iron, calcium, manganese and magnesium can be foam separated from acid solution by proper control of the independent variables. Reduction of residual surfactant concentration in the treated water and reduction of water entrained with the foam are two areas in need of further investigation.

Foam separation was tested on acid drainage, partially lime neutralized drainage and complete limestone neutralized drainage. Tests on model solutions indicate that treatment of raw acid drainage is most feasible at present.

Operating and capital costs are estimated for 0.1 and 1.0 MGD batch treatment plants.

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Treatment of Acid Mine Drainage

by

Horizons Incorporated
23800 Mercantile Road
Cleveland, Ohio 44122

for

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ABSTRACT

Basic experiments were conducted to establish the feasibility of foam fractionation in the treatment of acid coal mine drainage for the removal of the metal ions iron, calcium, manganese and magnesium. The independent variables controlling foam separation of metal ions were determined to be the concentration ratio of surfactant to iron, the air volume throughput, the foam drainage time, the total dissolved salt content and the type of surfactant used.

The major part of iron, calcium, manganese and magnesium can be foam separated from acid solution by proper control of the independent variables. Reduction of residual surfactant concentration in the treated water and reduction of water entrained with the foam are two areas in need of further investigation.

Foam separation was tested on acid drainage, partially lime neutralized drainage and complete limestone neutralized drainage. Tests on model solutions indicate that treatment of raw acid drainage is most feasible at present.

Operating and capital costs are estimated for 0.1 and 1.0 MGD batch treatment plants. Reduction of chemical costs through recovery and regeneration of surfactant is the major means for total cost reduction. Further investigation of methods for surfactant reuse are required. Significant capital cost reduction on a volume basis is estimated for 1.0 MGD in contrast to 0.1 MGD operation.

This report was submitted in fulfillment of Project 14010 DEE, Contract 14-12-496, under the sponsorship of the Federal Water Quality Administration.

Key Words:

Foam separation, acid coal mine drainage, metal ion removal, iron, calcium, manganese, magnesium, surfactant, treatment costs.

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SECTION I

CONCLUSIONS

The significant conclusions reached are as follows:

1. Iron, calcium, manganese, and magnesium can be accumulated in and removed from solution by the foams of selected surfactants under controlled conditions.
2. The independent variables controlling efficient batch operated foam separation of metal ions are:
    a. the concentration ratio of surfactant to metal
    b. the air sparging rate as related to the total air volume throughput and the bubble residence time in the liquid phase
    c. the foam drainage time
    d. the total dissolved solids in the liquid phase
    e. the chemical nature of the surfactant

3. The major parts of iron, calcium, manganese and magnesium can be removed from acid drainage accompanied by a significant residual surfactant concentration left in the treated solution and by a significant water loss from the solution to the foam.
4. Temperature in the range from 1 - 25°C has no apparent effect on the efficiency of foam separation of metal ions.
5. Anionic surfactants are more efficient for foam separation of metal ions.

6. Of the surfactants tested, ring substituted and unsubstituted aliphatic sulfonates have shown most promise for foam separation in acidic solution.

7. An increase in total dissolved solids, particularly calcium, tends to reduce the foam drainage time or foam persistence, thus reducing separation efficiency.

8. The particular surfactant can have a significant effect on the rate of foam drainage and, thus, on the amount of water loss and the efficiency of foam separation.

9. The effect of pH on foam separation of metal ions is not completely clear, except that a high enough pH to promote precipitation of ferric hydroxide results in decreased foam separation efficiency.

10. The surfactant concentration has two restraints for efficient foam separation: (1) it must be large enough to promote persistent foam formation, (2) it must be large enough to provide an adequate surfactant to metal ion concentration ratio.

11. Analysis of capital and operating cost estimates indicates that surfactant costs are significant for the batch process.

12. Methods to improve surfactant recovery, regeneration and reuse would significantly reduce process costs.

13. Methods to improve foam drainage would significantly improve treatment efficiency.

SECTION II

RECOMMENDATIONS

1. Methods to increase foam drainage efficiency should be investigated in order to reduce liquid entrainment in the foam. Design of special drainage apparatus and further screening for surfactants with efficient drainage characteristics are two such areas for investigation.

2. The present research on batch foam fractionation should be extended to potentially more efficient continuous flow operation with systematic evaluation of the controlling independent variables determined to date.

3. Methods to recover and regenerate surfactant should be further investigated. If surfactant consumption (loss) can be effectively reduced, then operational costs for the process would be reduced and the cost restriction on surfactants could be reduced. Surfactants specific to particular metal ion could be developed and cost-effectively applied.

4. The few tests conducted on synthetic and natural acid mine drainage should be extended since the effects of these complex solutions on foam separation are not completely clear.

SECTION III

INTRODUCTION

The problem is the economic treatment of mine drainage for the production of water meeting the quality standards as established by the states under the Federal Water Pollution Control Act. The treatment of mine drainage requires the removal of metal and nonmetal ions and the neutralization of sulfuric acid; the extent of treatment will depend on the end use of the purified water. Progressively greater purification will be required for water meeting the standards of industrial use, domestic use and the most stringent interstate stream water quality criteria, respectively.

Coal and coal wastes often contain pyritic minerals which through wet oxidation produce ferrous sulfate and sulfuric acid.

$$FeS_2 + H_2O + 3.5O_2 \rightarrow FeSO_4 + H_2SO_4$$

By further reaction with surrounding minerals, the solution can increase in chemical complexity. A typical mine drainage may contain calcium,manganese, magnesium, aluminum, silicon chloride, and sodium in addition to iron, sulfate and free acid.

Obviously, the most objectionable constituents ought to be removed from the mine drainage before it is permitted to mix with ground and surface waters. Several methods of purification have been used. They need not be discussed here. It is sufficient to state that none of these processes are considered perfect and that the need for a better treatment method still exists.

In the present work foam fractionation was the method selected to treat mine drainage. Foam fractionation has several inherent features which make it attractive for the treatment of mine drainage, namely, simplicity and economy combined with operation at ambient temperature and pressure. The foam fractionation process is based on the chemical composition of the surface layer of a solution being different from that of the bulk. For instance, the concentration of a component in the surface layer may be much greater than in the bulk of the liquid. If this layer is removed, the residual solution will contain less of the component.

The investigator is confronted with two problems: (1) how to accumulate the unwanted material in the surface layer, and (2) how to remove this layer.

(1) Surface tension differences are a common cause of the above accumulation. Let γ denote the surface tension, and c the concentration of a solution. If $d\gamma/dc$ is negative, that is, if surface tension decreases when concentration increases, then it is energetically advantageous for the system to accumulate the solute near the surface. Hence, the surface energy (and the total free energy) of the system is lowered when segregation takes place; thus, accumulation of the "surface-active" solute next to the surface is a spontaneous process. The thermodynamic basis for surface adsorption is given approximately by the simplified form of the Gibbs equation

$$-\frac{d\gamma}{dc} = \frac{RT}{c}\Gamma \qquad (1)$$

where Γ is the surface excess ($g \cdot cm^{-2}$) of a component with concentration c ($g \cdot cm^{-3}$) in the bulk liquid. R is the gas constant, and T is the absolute temperature.

In aqueous solutions of inorganic salts, such as ferrous sulfate, water is the surface-active ingredient. This means that the surface tension of these solutions increases when the salt concentration increases so that the surface layer contains less salt than an equal volume of the bulk liquid. However, if the liquid contains, in addition to the salt, a surfactant, the surfactant may transfer the inorganic ingredient into the surface layer. Suppose, for instance, that sodium dodecyl sulfate is the surfactant and $FeSO_4$ is the inorganic salt. The chemical reaction

$$2C_{11}H_{23}\cdot CH_2\cdot O\cdot SO_2\cdot ONa + FeSO_4 \rightleftharpoons$$
$$(C_{11}H_{23}\cdot CH_2\cdot O\cdot SO_2\cdot O)_2Fe + Na_2SO_4$$

is probable and the resulting ferrous dodecyl sulfate accumulates in the surface because it lowers the surface tension of the solution in the same manner as does sodium dodecyl sulfate.

The accumulation of surfactant and salt in the surface layer can be expressed quantitatively. Let Γ, measured in $g\cdot cm^{-2}$, be the surface excess of a component. Hence, the amount of this component present in a layer δ cm thick and of area A cm^2, is $A_o \delta c + A_o \Gamma$, where c is the concentration of the component in $g\cdot cm^{-3}$. If there were no segregation at the surface, this amount would have been $A_o \delta c$. The ratio of the two concentrations is given by

$$R = A_o \delta c + A_o \Gamma)/A_o \delta c = 1 + (\Gamma/\delta c). \tag{2}$$

In many instances of equilibrium adsorption, Γ is of the order of 10^{-9} g-mol$\cdot cm^{-2}$. If Γ is 10^{-6} cm and c is 10^{-6} g-mol$\cdot cm^{-3}$, then the above ratio is as high as 1001. This ratio is usually denoted as the accumulation ratio R.

(2) The surface layer of a liquid can be removed by mechanical skimming but foaming is a much simpler and more efficient method for separating the surface active component from the bulk liquid. As gas is bubbled through the liquid, adsorption of surfactant occurs at the liquid-gas interface. If the bubbles remain intact as they pass out of the bulk liquid, and if the foam remains stable without bursting or coalescing for at least several minutes, then physical separation of the component enriched foam provides an effective separation process. Thus it is obvious that since bubbles provide the surfaces for adsorption, more efficient separation would be achieved by maximizing the total bubble surface area passing through the bulk liquid.

Foam bubbles are usually distorted pentagonal dodecahedrons. To simplify the discussion of foams, assume them to be cubes with linear edges of ℓ . If δ is the thickness of the liquid film surrounding the gas phase, then the bubble surface area is $6\ell^2$ and the liquid volume in the bubble is approximately $6\ell^2\delta$. Foam films may be pictured as sandwiches in which a solution (whose composition is almost identical with that of the bulk solution) is confined between two (usually unimolecular) layers of surfactant. Let δ_1 be the thickness of each surfactant layer and δ_o the thickness of the liquid interlayer, so that $\delta = 2\delta_1 + \delta_o$. Assuming that the density of all materials involved is equal to that of water, the amount of the surfactant pertaining to one bubble is $6\ell^2(2\delta_1 + c\delta_o)$. The concentration (g·cm^{-3}) of the surfactant in the foam lamellae is $(2\delta_1 + c\delta_0)/(2\delta_1 + \delta_0)$. The ratio of this concentration to that (c) in the bulk solution is another expression of the accumulation ratio R.

$$R = \frac{2\delta_1 + c\delta_0}{c(2\delta_1 + \delta_0)} . \qquad (3)$$

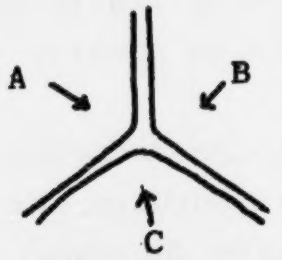
The purpose of deriving equation (3) is to show the dependence of efficient foam separation on the thickness δ_0 of the liquid interlayer in a foam film. If δ_0 is large, then relatively more liquid with essentially the concentration of the bulk solution is contained within the film. This reduces the efficiency of surfactant separation. When δ_0 is very small, the surfactant concentration in the film is almost equal to 1, and almost the whole film consists of surfactant. For example, if $c = 10^{-4}$ g·cm^{-3}, then $R = 10^4$. In contrast, if δ_0 is much greater than δ_1, then surfactant concentrations in the foam and in the bulk are almost equal, and R = 1.0.

The above considerations are only approximate because the thickness of the liquid surrounding a gas bubble in a foam is not constant. At the cross-line between three bubbles, a thicker liquid vein (now known as Plateau's border) exists, and a considerable fraction of the solution present in the foam is found in these veins. The semi-quantitative conclusions that R greatly depends on δ_0 are not invalidated by this refinement.

Both effects considered above, that is the accumulation of a component in the surface layer and the spatial separation of this layer in a foam, are time-dependent.

When a bubble forms in a surfactant solution, surfactant molecules (or ions) have to diffuse to the air-liquid interface before they can coat this boundary with an oriented unimolecular layer. If the bubble is released right under the horizontal surface of the bulk liquid, the time of ascent through the bulk liquid may be too short to achieve equilibrium adsorption at the bubble surface as described by the Gibbs equation (1). However, in the experiments reported here, no effect was noticed which could be attributed to an incomplete adsorption. Consequently, this complication is not considered further in the present report.

When a foam rises in a vertical tube a simultaneous liquid flow in the opposite direction takes place. This flow is known as foam drainage and is an important factor controlling the efficiency of foam separation. Foam drainage has two causes and two paths. One obvious cause is gravitation; the liquid is denser than air and, consequently, drains down. The other cause is related to surface tension. Figure 1 schematically represents a cross-section through three foam bubbles in contact.



Cross-Section through Three Foam Bubbles in Contact
FIGURE 1

A, B, and C are the gas volumes. The liquid films between them form three angles of 120° each. At the spots indicated by the arrows, the gas-liquid interfaces are concave to the gas phase. Consequently, the pressure in the liquid between the arrows (this space is a Plateau border) is less than elsewhere in the bubble wall. This pressure difference drives liquid toward and into Plateau's borders, in which downward flow then occurs.

Thus, a part of the liquid drains through Plateau borders. Another part flows in the lamellae between the relatively flat bubble walls. The relative importance of the two paths depends on the ratio of the lamellae thickness to the average diameter of the Plateau border. In many systems the lamellae are so thin that the Plateau borders are the main drainage channels. The Plateau borders, as seen in Figure 1, are not of circular cross-section, but an average radius r may be attributed to each. The volume rate ($cm^3 \cdot sec^{-1}$) of drainage is proportional to r^4, and thus is greatly dependent on the dimension of the liquid veins.

When the drainage times of two different surfactant solutions are compared, the difference may be due to the different values of the radii r. There is also another cause of difference. When the external layers of each foam film (whose thickness was denoted with δ_1 above) are nearly solid, the drainage takes more time than if the layers are more liquid-like. At given external conditions, the rate of drainage greatly depends on the properties of the surfactant used.

The volume rate of drainage decreases in time because the effective radius r of Plateau borders and the thickness δ_o of the liquid interlayer gradually decrease. In some instances it seems to stop when δ_o reaches the order of magnitude of 100 Å. Presumably, the mutual repulsion of electric double layers causes this interruption of drainage. If δ_o is near 100 Å, then it is nearly equal to the $2\delta_1$ value for many commercial foaming agents. If $\delta_o \approx 2\delta_1$, then R of equation (3) is approximately (1 + c)/2c. If, as in above example, $c = 10^{-4}\ g \cdot cm^{-3}$, then $R \approx 5000$.

The attainment of accumulation ratios of this magnitude usually is impossible in a foam because of bubble bursting. Each time a bubble wall breaks and the droplet formed mixes with the bulk solution, the accumulation ratio is decreased.

If considerable bursting starts when the bubbles are ϵ seconds old, then the drainage should not be continued longer than ϵ or even 0.5 ϵ seconds. Thus, the persistence (or lifetime) of the foam bubbles determines the duration of the drainage and, consequently, the highest accumulation ratio which can be achieved. Different surfactants produce foams with varying persistences. A high value of ϵ is a requisite property for a surfactant suitable for foam fractionation.

A complete discussion of the structure and drainage of foams is given by Bikerman (1).

SECTION IV

EXPERIMENTAL

1. Apparatus - Foam Tower

Compressed air from a cylinder was forced through a metering valve into a 20 liter glass jar, then through a purification and humidification system (sulfuric acid, sodium hydroxide, and water), a stopcock, a flowmeter, and a gas dispersing tube. The dispersing tube (Figure 2) usually was of "extra coarse" fritted glass with a nominal pore size of about 0.2 mm.

Figure 2 illustrates two types of foaming tower used in the experiments. A three-neck 2.5 liter flask (1) contained the solution to be foamed. Compressed air was introduced through one of the side tubes through the air dispersing device (2). The foam rose in the glass tower (3) which was graduated in 100 cm^3 intervals. The internal diameters of the tubes ranged from 30 to 114 mm. The lower part of each tube was narrow so that it could be inserted into the central opening of the flask (1). The vertical length of the tube was usually 50 cm. In early experiments, the foam tower was open at the

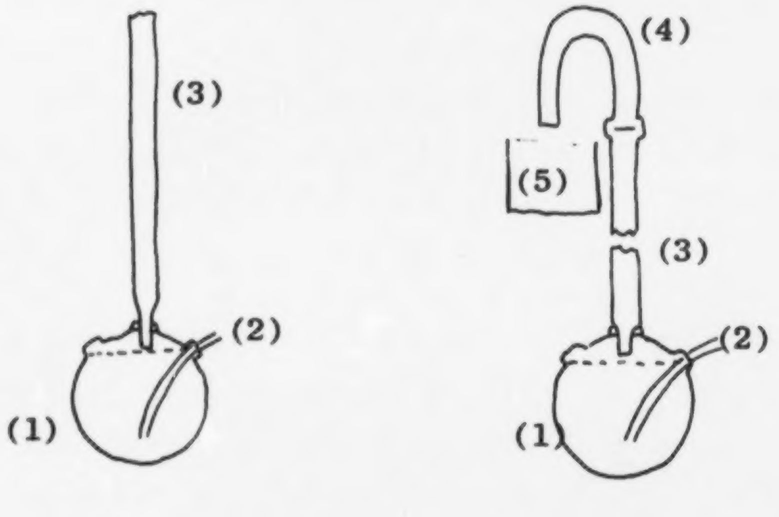


FIGURE 2 : Experimental Foam Tanks

upper end, and the foam rising above this end was cut off with a spatula and transferred to a container. In later tests, an inverted glass U-tube was mounted on the tower, and the foam flowed into the receptable (5).

The duration of drainage, the importance of which was emphasized in the Introduction, can be calculated from the flowmeter readings. The flowmeters used were calibrated for the experimental conditions and the readings translated into volume rates of air V $cm^3 \cdot sec^{-1}$. If S is the cross section (cm^2) of the foam tower, then V/S $cm \cdot sec^{-1}$ is the linear ascent rate of air. If the height of the tower is h cm, then hS/V sec is the time during which the bubbles exist and drain. Hence, the duration of drainage is hS/V.

Another simple way to measure the duration of drainage is direct observation of the ascent of selected bubbles visible through the glass tower. If $\Delta h/\Delta t$ is the linear rate of bubble ascent and h is the total height of the tower, then the duration of drainage is $h\Delta t/\Delta h$ sec. It is assumed in both methods that no significant bursting or coalescing of bubbles takes place.

The first method also implies that the air pressure in the bubble is identical with atmospheric pressure for which the flowmeter was calibrated. This assumption cannot be exact because the bubble walls usually are curved, and capillary pressure would increase the pressure in each bubble. A simple calculation shows, however, that this complication is negligible. The equation for the change in capillary pressure Δp is

$$\Delta p = 2\gamma/r$$

where γ is the surface tension of the solution and r is the radius of curvature of the bubble walls. The radius r is much greater than the length ℓ of a simplified cubical bubble as defined in the Introduction. In the experiments being reported, ℓ rarely was shorter than 0.1 cm. Since γ usually was near 30 $g\cdot sec^{-2}$, it follows that Δp generally was less than 600 $g\cdot cm^{-1} sec^{-2}$. Since the average atmospheric pressure is 10 $g\cdot cm^{-1} sec^{2}$, the pressure inside a bubble was at most only 0.06% greater than outside.

2. Procedure - Operation of Foam Tower

The solution to be foamed was prepared and placed in the foaming flask. The dissolution of the inorganic salts in water offered no difficulty but it was necessary to stir the foaming agent for several minutes to obtain a dispersion which appeared uniform. It appears that the surfactant concentrations used in this study were generally above the critical micells concentrations so that colloidal particles were present. An aliquot of the initial solution was withdrawn for analyses. The flask and remaining solution was weighed and the total weight W_o recorded.

The 20-liter jar was filled with air at a pressure of 4 - 8 psi. The stopcock between the jar and the flowmeter was opened to a predetermined reading. The gas dispersing tube was immersed in the flask. Conspicuous foam bubbles were selected in the rising foam and their rates of ascent measured using the graduated column and a stopwatch.

After a predetermined interval, foaming was interrupted and the foam present in the tower was permitted to drain and collapse for 30 minutes. When the amount of foam produced was small, the foam present in the tower was pushed or blown into the receptacle. In either case, the total weight of the flask and contents W_1 after foaming was recorded. After W_1 was ascertained, foaming was resumed. After a predetermined time interval, the second foam was collected and its weight was determined by weighing the flask with the remaining liquid. Subsequently, the collection of the third foam was started, and so on until foaming was ceased.

Theoretically, $W_1 - W_0$ was the weight of the wet foam fully corrected for evaporation. If the wet foam was weighed, the mass W_f obtained was smaller than $W_1 - W_0$ because of evaporation. The difference between W_f and $W_1 - W_0$ has not been systematically investigated.

In some experiments an additional foam collection was performed. When the foaming ability of the bulk liquid was reduced such that at a given rate gas flow no foam rose over the top of the tower, then the residual liquid was transferred from the 3-neck flask into a large beaker. The gas dispersing tube was immersed in the beaker and an inverted glass funnel was placed above the liquid so that its lower rim was about 1 cm above the surface of the liquid (Figure 3). The stem of the funnel was attached by rubber tubing into a partially evacuated flask. The foam formed in the beaker was sucked up into the funnel and collected in the flask. Samples of all foam and liquid fractions were collected for analyses.

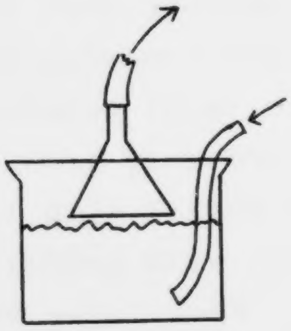


FIGURE 3

Beaker Foaming Apparatus

3. Analytical Methods

Initial solution, foam and residual solution samples were analyzed for water, surfactant, iron, calcium, manganese, magnesium and sulfuric acid as required by the chemical composition and purpose of the various foaming experiments. The methods used are referenced below.

(1) Water. Since water was always present in much greater amounts than the dissolved components, its quantity was determined simply by weighing. When the mass of an initial solution was reduced by foaming from $W_0 - W_1$ grams (see p. 11), it was permissible to ascribe the weight loss $W_0 - W_1$ to water removed with the foam.

(2) Surfactant. Surfactants analyzed were sodium or ammonium salts of ring substituted and non-substituted aliphatic sulfonates and can be represented by the formula $R \cdot O \cdot SO_2 \cdot ONa$. These surfactants form colored complexes with ionic dyes and can be determined colorimetrically (2).

(3) Iron. Three methods were used to determine Fe depending on the concentration of surfactant present. When small relative amounts of surfactant were present, iron was determined colorimetrically as Fe(II) with 1,10-phenanthroline after reduction with hydroxylamine hydrochloride solution (3). When large relative amounts of surfactant were present, iron was determined colorimetrically as Fe(III) with potassium thiocyanate after oxidation of surfactant with nitric and perchloric acids and oxidation of iron with ammonium persulfate (4).

Alternately, total iron was determined directly using an atomic absorption spectrophotometer (AA) without destruction of surfactant (5). Towards the end of this contract all iron determinations were run on the AA.

(4) Calcium. Three methods were used to determine Ca depending on the relative amounts of surfactant and iron present. When the ratio of calcium to iron was large and the relative amounts of surfactant small, Ca was determined directly by EDTA titration using "Calcein"* indicator without prior oxidation of the surfactant (6). When the ratio of calcium to iron was small or moderate, calcium was determined colorimetrically with potassium permanganate after oxidation of the surfactant and separation of iron and calcium by oxalate precipitation of calcium (4). Toward the end of the contract, calcium was determined directly with the AA without eliminating either surfactant or iron (5).

(5) Manganese. Manganese was determined colorimetrically as potassium permanganate after destruction of surfactant with sulfuric and nitric acids and after oxidation of manganese with potassium periodate (4).

(6) Magnesium. Magnesium was determined directly on the AA without prior treatment (5).

(7) Sulfuric Acid. Sulfuric acid was determined by titration with standard sodium hydroxide using methyl orange as the indicator (4).

(8) pH. pH values were determined with a standard temperature corrected meter, glass electrode and calomel reference electrode.

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* Mention of commercial products is for clarification only and does not imply endorsement by the Federal Water Quality Administration.

SECTION V

RESULTS AND DISCUSSION

1. Surfactant Screening Tests

As noted in the Introduction, the ability of a surfactant to produce a persistent foam is requisite for efficient foam separation. Thus the first screening of surfactants was for foam production and persistence under chemical conditions similar to acid mine drainage. The surfactants tested were restricted to inexpensive compounds available in commercial quantities. The compositions of many of the surfactant compounds were proprietary, and thus they contained unknown constituents in unknown amounts.

The surfactants tested are listed in Table I with brief comments on the test results. Those surfactants which produced persistent foams were tested for accumulation of metal ions in the foams. Some of these tests were conducted under contracts with the Office of Saline Water (7)(8). In general, the non-ionic surfactants (Deriphat 160, Deriphat 170C, Arlacel 60, Brij 58, Tween 60, Emulphogene BC-720 and Igepon AC-78) accumulate iron and manganese under acid conditions to a much smaller extent than the anionic surfactants (sodium dodecyl sulfate, Alipal CO-433, Alipal CD-128 and Alipal EO-526) (8). It was found that iron and manganese are more readily concentrated in the foam of Alipal EO-526 than in those of sodium dodecyl sulfate or Deriphat 170C (8). It appears that this superior accumulation is partly, or mainly, a result of the more rapid drainage of Alipal foams (8). Alipal CD-128 is a new surfactant of similar character to Alipal EO-526 except that it is claimed by the manufacturer to be biodegradable (Table I).

Alipal EO-526, Alipal CD-128 and sodium dodecyl sulfate were chosen on the basis of the above described tests for the foam separation tests to follow. As a result of the foam separation tests, it is concluded that other factors, such as foam

TABLE I

Surfactant Screening Tests

Surfactant Compound*	Source*	Nature	Test Results
Deriphat 160	General Mills Inc.	disodium N-lauryl- -iminodipropionate	Required high air rate to produce foam. Difficult to dissolve in H_2O.
Deriphat 170C	General Mills Inc.	(mainly) N-laury - myristil-β- aminopropionic acid	Similar to Deriphat 160
Arlacel 60	Atlas Chemical Industries	sorbitan monostearate	Required very high air rate to produce foam.
Brij 58	Atlas Chemical Industries	polyoxyethylene hexadecyl ether	Satisfactory foam production and persistence.
Tween 60	Atlas Chemical Industries	a polysorbate	Satisfactory foam production and persistence.
Emulphogene BC-720	General Analine & Film Corp.	tridecylorypoly (ethylenoxy)ethanol	Low foam persistence.
Igepon AC-78	General Aniline & Film Corp.	coconut acid ester of sodium isethionate	Low foam persistence.
Sodium dodecyl sulfate	duPont de Nemours Corp.	sodium lauryl sulfate	Good foam production and persistence; slow foam drainage.
Alipal CD-433	General Aniline & Film Corp.	lower homolog of Alipal EO-526	Satisfactory foam production and persistence.

TABLE I (continued)

Surfactant Compound*	Source*	Nature	Test Results
Alipal CD-128	General Analine & Film Corp.	ammonium salt similar to Alipal EO-526 but of aliphatic nature	Good foam production and persistence.
Alipal EO-526	General Aniline & Film Corp.	sodium salt of a sulfated alkylphenoxy poly(ethyleneoxy) ethanol	Good foam production and persistence.

* Mention of commercial products is for clarification only and does not imply endorsement by the Federal Water Quality Administration.

drainage time, air sparging rate and surfactant to metal concentration ratio, are more important for effective metal separation than any of the three surfactants.

None of the surfactants tested showed specificity for any of the metals tested. Since the choice of surfactants was limited to inexpensive, commercially available compounds, the choice was limited. It is evident from our work that to find a specific surfactant will require testing of a less restricted class of compounds and, possibly, synthesis of special compounds. It would be expected that such a specific compound would be expensive and not immediately available for foam treatment of acid mine drainage.

2. Foam Separation Tests

The usual acid mine drainage contains two highly objectionable components, namely iron and sulfuric acid. In addition, significant amounts of calcium, manganese and magnesium are often present. In principle it is possible to foam separate iron from sulfuric acid and neutralize the acid as a secondary process. In contrast, the acid could be neutralized prior to foam removal of iron. Both these possibilities were investigated. In theory, if a surfactant exists which combines with one metal in preference to another, then the two metals could be selectively separated by foaming. The results of the surfactant tests exposed no such selective surfactants within the class of inexpensive, commercially available detergents investigated.

In the first set of experiments the amounts of ferrous sulfate and sulfuric acid in the initial solutions were equivalent. These experiments were conducted with simplified acid drainage to define feasibility for foam separation of iron in acid media. The second set of experiments tested the removal of iron and calcium from partially neutralized solutions of simplified acid mine drainage. The third set of experiments investigated the removal of iron and calcium after limestone neutralization of simplified solutions of acid mine drainage. In addition the effect of temperature on foam separation was investigated. The fourth set of experiments investigate the removal of manganese and iron from simplified acid mine drainage. The fifth set of experiments investigate the foam separation of iron calcium and magnesium from synthetic and real acid mine water.

(1) Foam Separation of Iron from Acid Solutions

In these tests the amounts of ferrous sulfate and sulfuric acid in the initial solutions were equivalent. The surfactants used were commercial grade sodium dodecyl sulfate (NDS), Alipal CD-128 and Alipal EO-526. The operating parameters, analytical results and dependent variables for the 18 experiments in this set are presented in Tables II, III and IV.

The Effect of the Surfactant: Iron Concentration Ratio

It is evident from the data in Tables II and III that ferrous iron can be successfully separated from sulfuric acid solutions by foaming. Figure 4 shows the dependence of iron removal on the concentration ratio of surfactant to iron. As the trend line indicates, iron removal increases with the ratio. It would be expected that increasing the ratio above a certain value should have negligible effect on iron removal. The data in Figure 4 tends to suggest this, as the trend line could be drawn with a slope approaching zero as the ratio increases.

At present it is not known what compound of iron is present in the walls of foam lamellae when sodium dodecyl sulfate or an Alipal is the foaming agent. It is possible that this compound is simply the ferrous salt of the surfactant anion. The three surfactants used in the foam separation tests may be represented by the formula RSO_4Na. A salt of this type is likely to react with ferrous sulfate according to the equation

TABLE II

Experiment No.	1	2	3	4	5	6	7	8	9
Air Rate, $cm^3 \cdot sec$	3	6	6	3	6	3	6	6	6
Foaming Time, min	124	70	195	185	125	135	120	95	95
Drainage Time, sec	2200	1100	1100	2200	1100	2200	1100	1100	1100
Initial Solution Weight, g	2007	2007	2070	2200	2200	2070	2070	2007	2070
Surfactant	NDS	NDS	NDS	NDS	NDS	NDS	NDS	CD-128	CD-128
Initial Surfactant Concentration, ppm	984	1019	873	840	815	900	882	1050	1030
Initial Fe Concentration, ppm	9.4	9.4	101	286	277	976	1030	12.5	103
Initial $\frac{\text{Surfactant}}{\text{Fe}}$	105	108	9.6	2.9	2.9	0.92	0.86	84.0	10.0
Initial pH	5.1	5.1	3.25	2.61	2.62	2.50	2.50	3.64	2.75
Residual Solution Weight, g	1997	1953	2018	2198	2174	2069	2021	1957	1980
Water Loss with Foam, %	0.50	2.7	2.5	0.091	1.2	0.048	2.4	2.5	4.3
Residual Surfactant Concentration, ppm	813	838	610	700	720	770	682	1040	880
Residual Fe Concentration, ppm	1.6	2.1	76	264	254	940	950	7.2	99
Residual pH	4.8	5.0	3.22	2.82	2.82	2.52	2.51	3.59	2.80
Foam Weight, g	10	54	52	2.1	26	1.3	49	50	90
Fe Removed, %	83	78	27	8	9	4	10	44	8
Surfactant Removed, %	18	20	32	17	13	15	25	3	18
Accumulation Ratio:									
Foam:									
Fe	260	49	8	30	6	34	2.2	17	1.7
Surfactant	19	2.5	11	102	12	140	9.2	1.9	-
H_2SO_4	-	-	2.4	6	0.7	1.3	0.12	-	-
Residual Solution:									
Fe	0.2	0.2	0.7	0.9	0.96	0.9	0.92	0.6	0.96
Surfactant	0.8	0.8	0.7	0.8	0.9	0.86	0.77	0.99	0.85
H_2SO_4	-	-	0.9	0.9	0.9	1.0	0.95	-	-

TABLE III

Experiment No.	10	11	12	13	14	15	16	17
Air Rate, cm³·sec	6	6	6	6	6	6	6	6
Foaming Time, min	120	145	120	240	240	180	180	180
Drainage Time, sec	1100	1100	1100	1100	1100	1100	1100	1100
Initial Solution Weight, g	2070	2070	2200	2200	2200	2070	2200	2200
Surfactant	EO-526	EO-526	EO-526	CD-128	CD-128	EO-526	EO-526	EO-526
Initial Surfactant Concentration, ppm	1670	1260	1160	850	1700	980	4830	2380
Initial Fe Concentration, ppm	11.5	90	300	245	279	950	300	288
Initial $\frac{\text{Surfactant}}{\text{Fe}}$	145	14	3.9	3.5	6.1	1.0	16	8.3
Initial pH	3.70	2.85	-	2.4	2.3	2.0	2.25	2.30
Residual Solution Weight, g	1985	2048	2179	2110	1936	2046	2132	2140
Water Loss with Foam, %	4.1	1.1	0.95	4.1	1.2	1.2	3.1	2.7
Residual Surfactant Concentration, ppm	1200	400	570	630	1350	500	4080	1750
Residual Fe Concentration, ppm	3.9	76	290	176	-	840	278	243
Residual pH	3.72	2.90	-	2.4	2.1	1.9	2.20	2.20
Foam Weight, g	22	22	21	90	264	24	68	60
Fe Removed, %	66	17	4	31	-	13	10	18
Surfactant Removed, %	29	69	51	29	30	50	18	29
Accumulation Ratio:								
Foam:								
Fe	48	6	3.4	1	0.5	1.7	1.9	2.2
Surfactant	2	30	19	8	1.6	33	3.9	9.4
H_2SO_4	-	-	-	0.04	-	1.2	1.3	1.3
Residual Solution:								
Fe	0.34	0.9	0.97	0.7	-	0.4	0.93	0.8
Surfactant	0.7	0.3	0.5	0.7	0.8	0.5	0.84	0.7
H_2SO_4	-	-	-	1.2	-	1.0	1.0	1.0

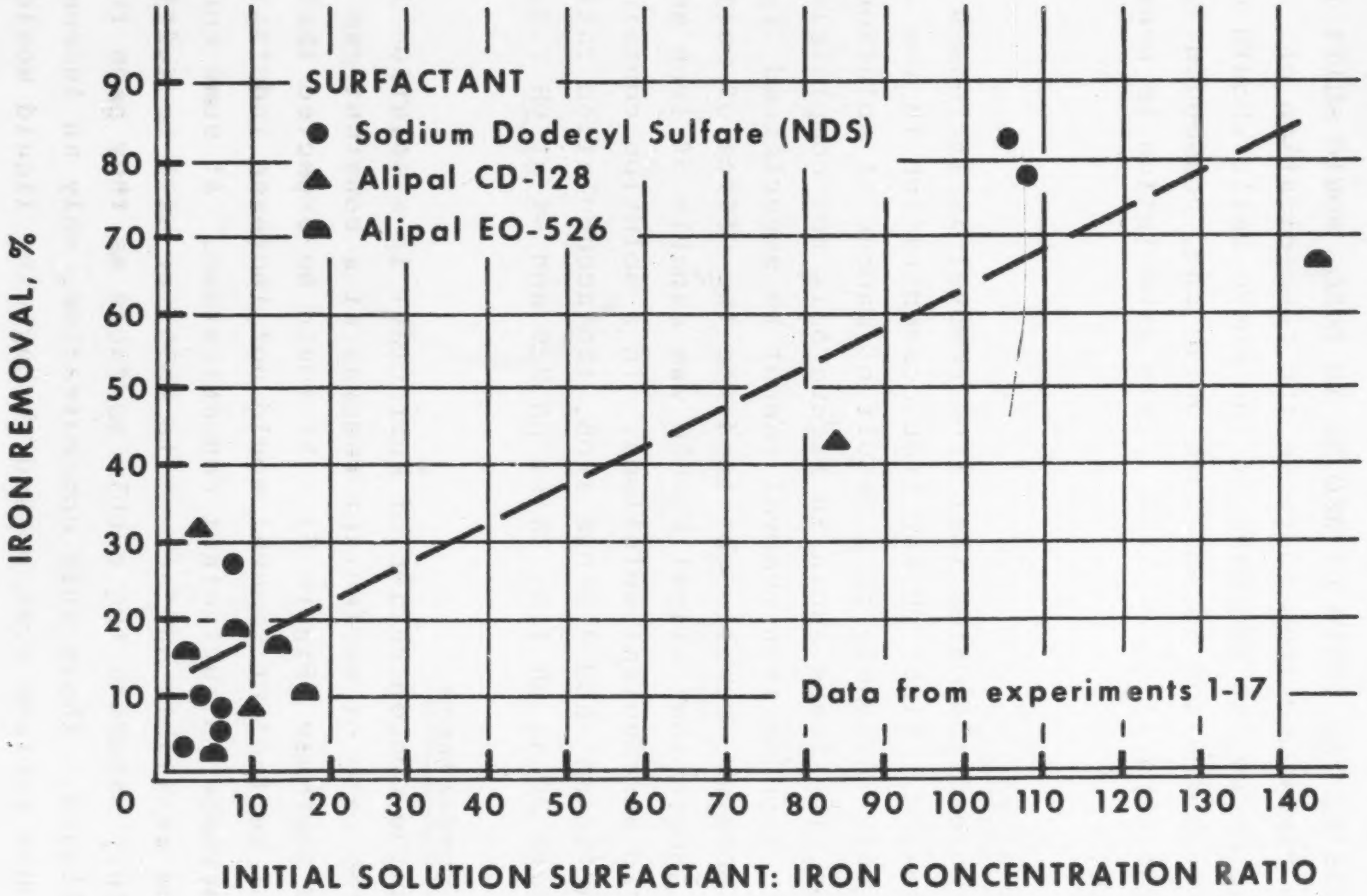

FIGURE 4 EFFECT OF SURFACTANT: IRON RATIO ON FOAM SEPARATION OF IRON

$$2RSO_4Na + FeSO_4 \rightleftharpoons (RSO_4)_2Fe + Na_2SO_4.$$

If such an equilibrium really is established, it may be expected that increasing the ratio of RSO_4Na to $FeSO_4$ would shift it toward the right and thus increase the concentration of $(RSO_4)_2Fe$. Hence, an increase in the above ratio should raise the iron concentration in the foam walls and, consequently, improve foam separation of iron. This expectation is proved in Figure 4.

The Effect of pH

Figure 5 indicates that iron removal is increased as pH is increased. Since pH and iron concentration in the initial solutions vary inversely as a result of manner of solution preparation, the trend shown in Figure 5 is not completely clear. The effect of pH on iron removal cannot be ascertained from these results. However, results obtained for the Office of Saline Water (8) showed that Alipal EO-526 was capable of iron separation in acid and neutral solutions. In a solution containing 590 ppm surfactant and 4.5 ppm iron, the accumulation ratios for iron were 20 at pH 1.9, 13 at pH 2.9 and 44 at pH 7.3.

Effect of Surfactants

As the concentration of surfactant in a solution is increased, the rate of surfactant removal at a constant gas rate is seen to increase (Figure 6). It would be expected that the rate of surfactant removal would not increase indefinitely with an increase in surfactant concentration. At some concentration the available surfactant in solution will be sufficient to completely saturate the bubble surfaces as they pass through the bulk liquid. Above this concentration, only an increase in the bubble surface area passed through the liquid would

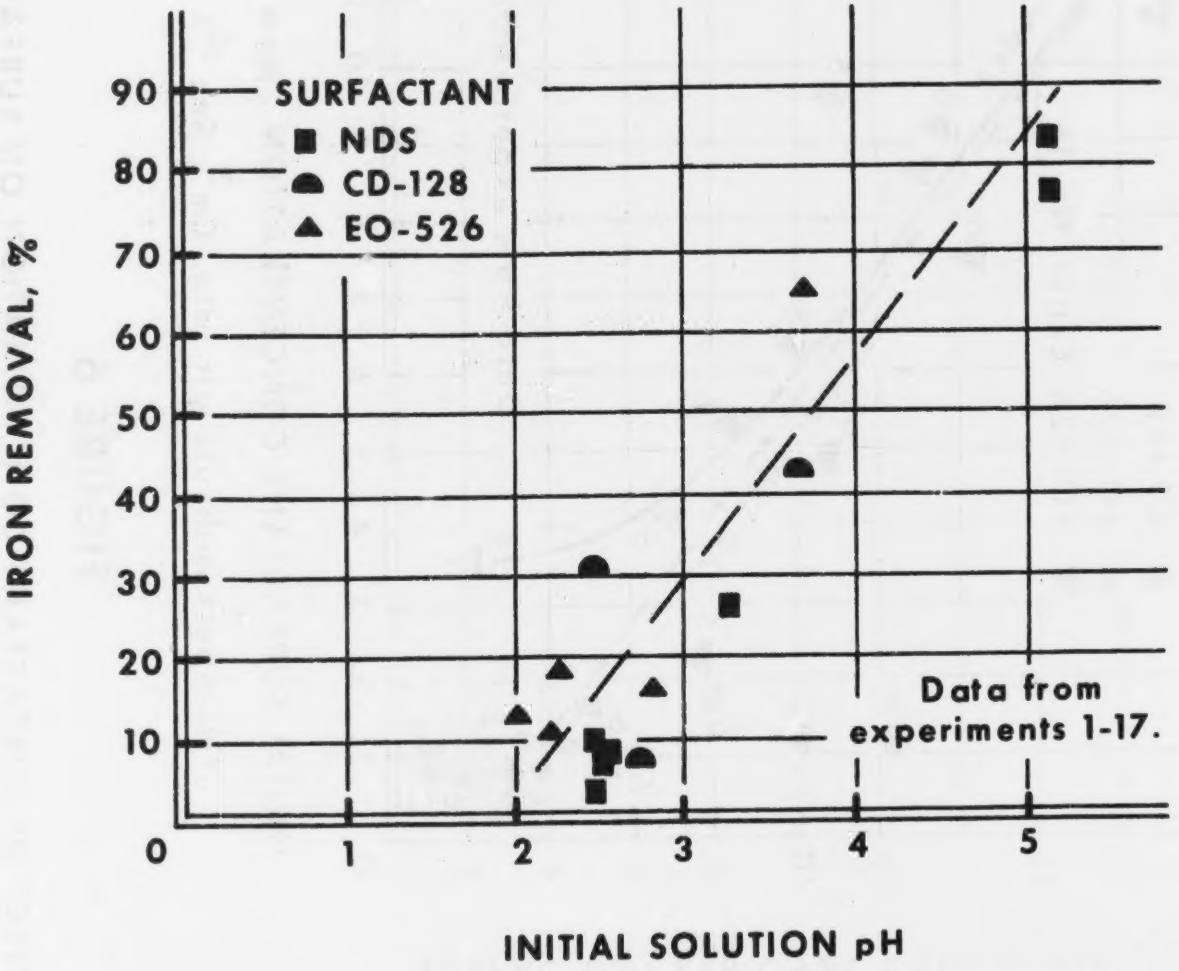

FIGURE 5 EFFECT OF pH ON IRON REMOVAL

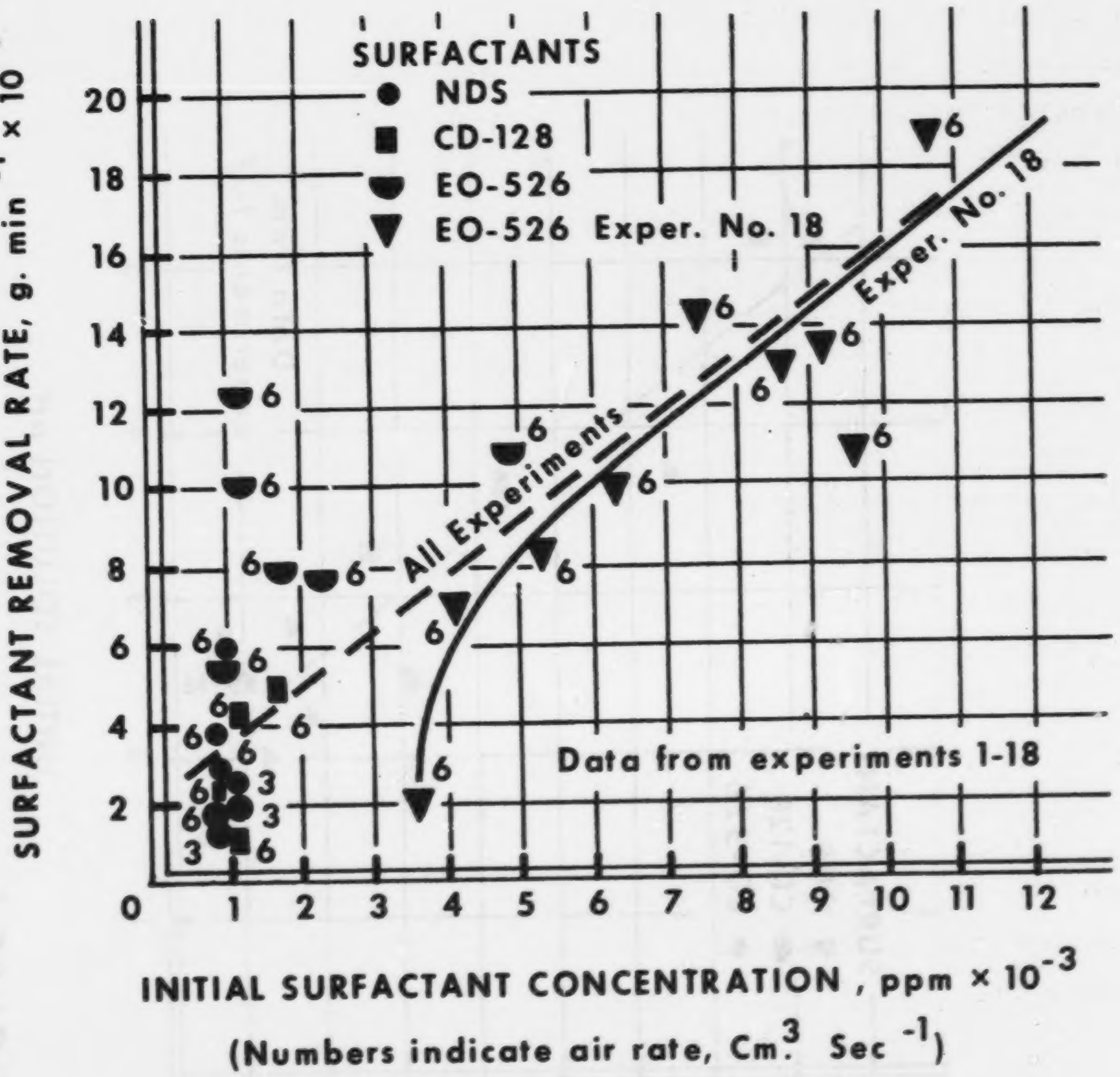

FIGURE 6

EFFECT OF SURFACTANT CONCENTRATION ON SURFACTANT REMOVAL RATE increase the rate of surfactant removal. Also, if the critical micelle concentration for the surfactant was surpassed, excess surfactant would not increase its removal rate. The fact that a minimum surfactant concentration is required to simply sustain a persistent foam is indicated in Figure 6. A surfactant concentration much below about 800 ppm is inadequate for foam separation. The results of the first 18 experiments (Figures 4 and 5) indicate no difference among the three foaming agents as far as iron removal is concerned.

The Effect of Drainage Time

The main effect of increased foam drainage is a reduction in the volume or weight of the foam collected. Figure 7 shows that for a given surfactant:iron concentration ratio the volume reduction factor (defined as the volume of initial solution divided by that of the collapsed foam) increases with drainage time. The percentage removal of iron is neither systematically or significantly affected by drainage time.

Multiple Foaming Experiment - Experiment 18

In this test 9 foam fractions were collected. After the ninth foam the residual solution was foamed in a beaker, and the foam was collected by suction as shown in Figure 3. The operating parameters and analytical results are shown in Table IV.

From the experimental data, the rate of iron removal can be calculated as a function of the surfactant:iron concentration ratio (Figure 8). Figures 8 and 4 are similar, as they indicate that the percentage removal and removal rate for iron are strongly dependent on the surfactant:iron concentration ratio. As discussed previously (p.22), the removal rate will not increase indefinitely with the surfactant:iron ratio. However, for the iron and surfactant concentrations used, the above conclusion is valid.

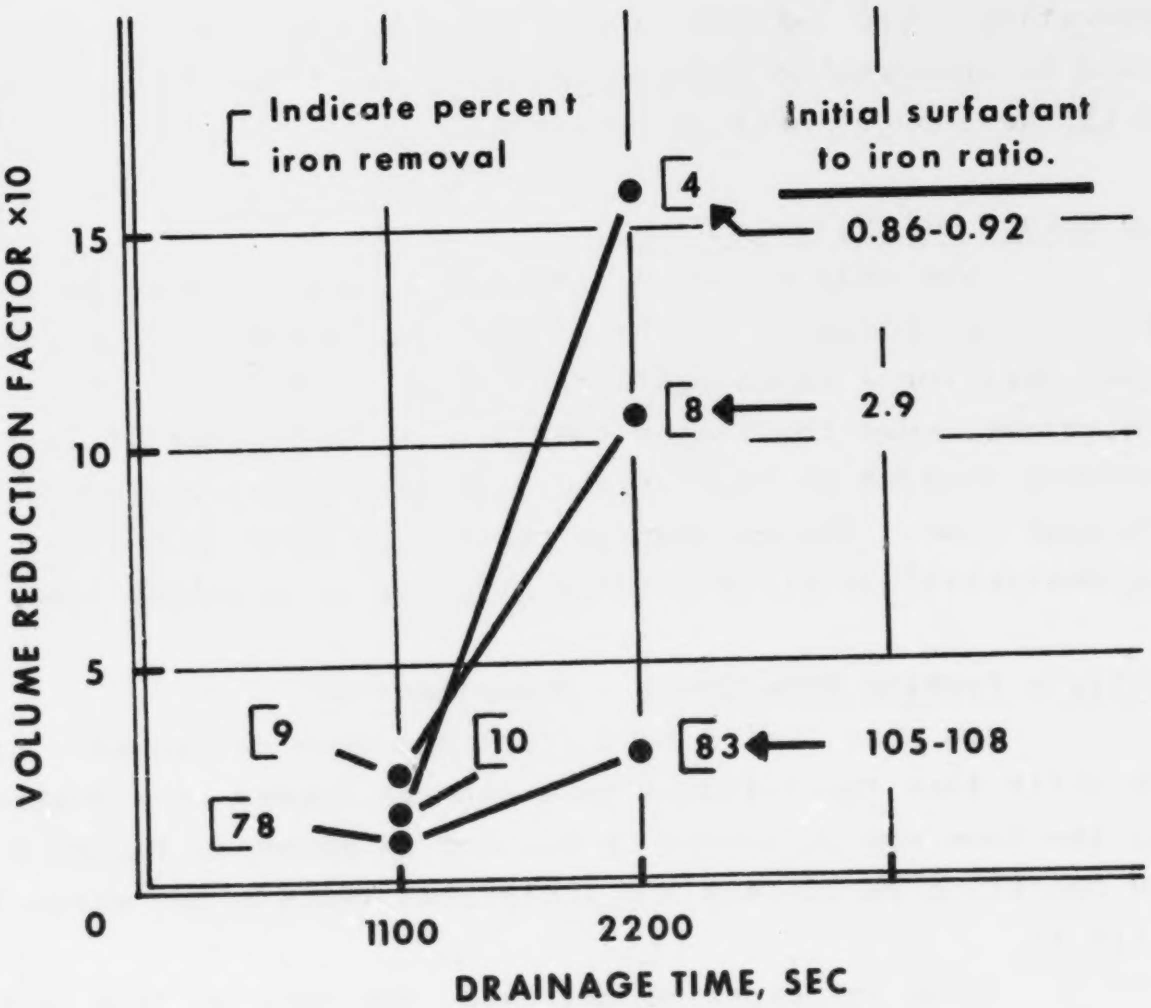

FIGURE 7
EFFECT OF DRAINAGE TIME AND INITIAL SURFACTANT: IRON RATIO ON VOLUME REDUCTION FACTOR
(Volume reduction factor is the ratio of the initial solution volume to the collapsed foam volume.)

TABLE IV

Experiment 18

Air Rate, 6 $cm^3 \cdot sec^{-1}$; Drainage Time, 1100 sec; Surfactant, Alipal EO-526

			Concentration					Cumulative	
	Foaming Time, min	Weight, g	Surfactant, ppm	Fe, ppm	Acid,	Fe Removal %	Surfactant Removal, %	Fe Removal, %	Surfactant Removal, %
Initial Solution	-	2220	10760	277	570	-	-	-	-
First Foam	185	77	45500	880	890	11.7	16.3	11.7	16.3
Second Foam	205	164	13700	270	700	7.7	10.4	19.4	26.7
Third Foam	185	129	19400	480	540	10.8	11.7	30.2	38.4
Fourth Foam	205	109	24700	450	840	8.5	12.6	38.7	51.0
Fifth Foam	200	113	25400	440	810	8.6	13.4	47.3	64.4
Sixth Foam	195	97	20000	470	790	7.9	9.0	55.2	73.4
Seventh Foam	245	97	21300	480	890	8.1	9.6	63.3	83.0
Eighth Foam	150	44.5	22700	490	730	3.8	4.7	67.1	87.7
Ninth Foam	125	16.5	19700	820	1030	2.3	1.5	69.4	89.2
Residual Solution	-	-	1700	130	360	-	-	69.4	89.2
Beaker Foam	70*	174	600	300	500	9.1	0.49	78.5	89.7
Final Residual Solution	-	-	260	100	360	-	-	78.5	89.7

Water loss with foam was 38% through the ninth foam and 46% including the beaker foam.

* Air rate, 62 $cm^3 \cdot sec^{-1}$

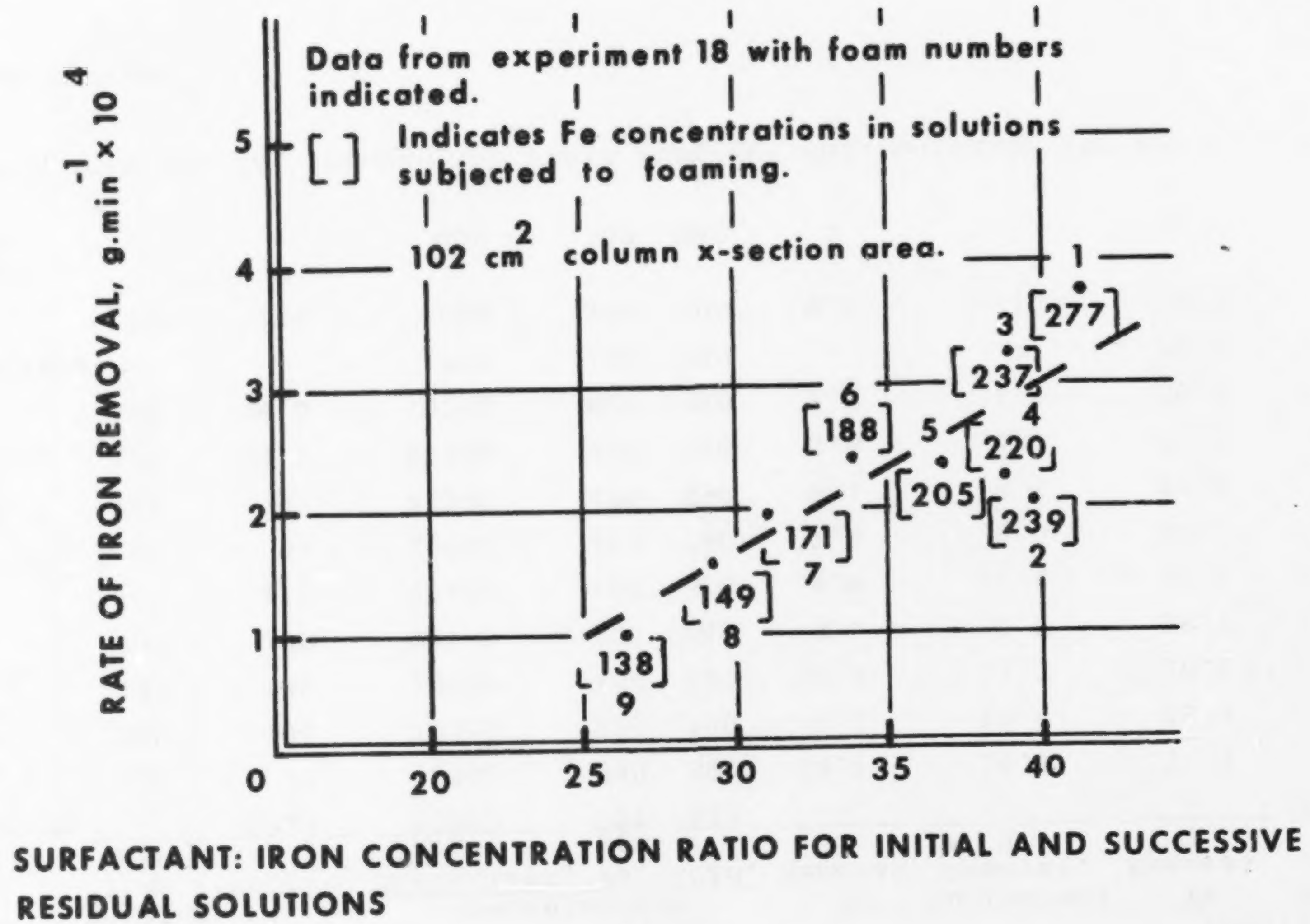

FIGURE 8

Rate of iron removal as a function of the surfactant: Iron ratio

(2) Foam Separation of Iron and Calcium from Partially Neutralized Solutions

Because of the low solubility of ferric hydroxide, it is likely to precipitate whenever the pH exceeds 4.0. Consequently, a neutral solution of ferrous or ferric ions is unstable. When acid mine drainage contains ferrous sulfate and sulfuric acid and when the acid is converted into a neutral sulfate (such as calcium sulfate of sodium sulfate), a precipitate or a colloidal solution of ferric hydroxide is obtained. However, it is possible to neutralize the main part of sulfuric acid and to stop before the pH reaches or exceeds 4.0. If lime is the base used for neutralization, a slightly acid mixture of ferrous sulfate and calcium sulfate results.

Contrary to sulfuric acid, calcium sulfate is poorly soluble in water. The solubility of gypsum little depends on temperature and is equal to about 2.1 g of anhydrous $CaSO_4$ in 1 kg of water. As 136 g of $CaSO_4$ are obtained from 98 g of sulfuric acid, the above solubility corresponds to the concentration of 1.5 g of H_2SO_4 in 1 kg. Thus, when there are more than 1500 ppm of sulfuric acid in the liquid treated with lime, the liquid after treatment will be a nearly saturated solution of gypsum. If the initial liquid is less concentrated, no sediment will occur but the solution submitted to foaming will contain $CaSO_4$ instead of H_2SO_4.

It was necessary to know how this substitution would affect foam fractionation. If the foam separation of iron is enhanced in the presence of $CaSO_4$ then it might be advisable to neutralize the mine discharge before submitting the filtrate to foam fractionation. In contrast, if the accumulation ratios are lowered by substituting $CaSO_4$ for H_2SO_4, then the foam fractionation treatment would have to precede the neutralization step.

Twenty-five experiments (Nos. 19-33) were conducted to determine the effect of partial neutralization on the foam separation of iron and calcium. As the sulfuric acid concentration in the mine drainage may be both higher and lower than 1500 ppm, both saturated and unsaturated gypsum solutions were tested as a vehicle for ferrous sulfate. The experimental details are presented in Appendix A.

The effect of partial lime neutralization and increased calcium on the foaming process is evident through comparison of experiments 10 and 29. In both, the calculated concentration of Alipal CD-128 was 1000 ppm and the calculated concentration of ferrous ion was 10 ppm; the first solution also contained a small amount of sulfuric acid while the second was a saturated solution of gypsum. Experiment 10, a drainage time of 1100 sec was maintained without any difficulty, but in the gypsum solution no drainage longer than 250 seconds could be achieved. A similar difference is observed in experiment 2 and 21, in which sodium dodecyl sulfate was the foaming agent. Table V lists the respective accumulation ratios.

TABLE V

Comparison of Foam Separation in Sulfuric Acid and Gypsum Solutions

	In 0.00035 N H_2SO_4 Drainage: 1100 sec	In Saturated Gypsum Solution Drainage: 250→340 sec
Accumulation Ratio for Iron		
NDS	49	4
Alipal	48	1

The ratio of calcium to iron in the experiments 21 and 29 was 62:1. If this ratio is much less, the depressing effect of calcium naturally is less pronounced. This can be seen by comparing experiments 5 and 24. Each initial solution contained about 1000 ppm of sodium dodecyl sulfate and 275 ppm of ferrous iron; in experiment 5 the matrix was 0.1 N H_2SO_4 and in experiment 24 150 ppm of calcium was present. This calcium concentration was so low that drainage time could be increased to 1200 seconds, so that it was nearly equal to the drainage time in experiment 5 (1100 seconds). The accumulation ratio for iron was 6 in dilute sulfuric acid and 2 in gypsum solution. When Alipal CD-128 was used instead of sodium dodecyl sulfate in otherwise identical experiments (see experiments 13 and 30), the accumulation ratio was near 1 in both acid and gypsum solutions. It must be concluded that no benefit is realized by partial neutralization with lime before foaming.

(3) Foam Separation of Iron and Calcium after Limestone Neutralization

Presumably, acid mine water will eventually have to be neutralized. Since calcium carbonate is an abundant material and is suitable for neutralization, it has potential wide use. In the reaction

$$H_2SO_4 + CaCO_3 = CaSO_4 + H_2O + CO_2$$

gaseous carbon dioxide is liberated. The question arises whether CO_2 can be substituted, at least in part, for the sparging air.

One mole of sulfuric acid produces 1 mole of carbon dioxide which, at the standard temperature and pressure, occupies about 22 liters. Ten millimoles of sulfuric acid would thus produce about 220 cm^3 of CO_2. This volume can be compared with the volume of air used for foaming a similar solution. In experiment 16, 68 g of foam were collected after injecting air for 180 minutes at the rate of 6 $cm^3 \cdot sec^{-1}$ for a total volume of 64800 cm^3. By calculation, substituting 220 cm^3 of CO_2 for an equal volume of air would not yield a considerable savings. Nevertheless, tests were made. It was found that, at the low concentrations of sulfuric acid used, the rate of evolution of CO_2 was too low to be useful.

In previous experiments, iron was removed by foaming without any significant alteration in the acid content. If free sulfuric acid is not permitted in treated drainage, neutralization of the acid would be necessary as a secondary step subsequent to foaming. In principle, both steps can be performed simultaneously. Base can be added to the acid drainage as sparging is begun. Alternately, the acid drainage could be neutralized prior to foaming.

Thirteen experiments (Nos. 34-46) were conducted to determine the effect of limestone neutralization on foam separation of iron and calcium. The practicality of simultaneous neutralization and foam separation and of neutralization prior to foam separation were investigated. The effect of temperatures to near freezing were investigated. The experimental details are presented in Appendix B.

In the experiments on foam separation of colloidal ferric hydroxide the accumulation ratios never exceeded 5. The separation of colloidal ferric hydroxide was unsuccessful because the foaming conditions used were designed to operate with soluble ions. Colloidal iron can be removed effectively in systems designed to do so (9)(10)(11)(12).

The results of foaming colloidal solutions were not always reproducible. Foaming was usually conducted soon after neutralization of sulfuric acid with calcium carbonate when oxidation of ferrous iron and formation of particulate ferric hydroxide were in process. Thus the chemical and physical nature of the solution (e.g., the ferrous to ferric iron ratio and the average particle size) varied from hour to hour and from test to test.

Neutralization prior to foaming causes additional load on the foam separation process because of the additional metal ions introduced. The oxidation of ferrous iron and the formation of ferric hydroxide increases the amount of base required for neutralization. For every mole of ferrous iron oxidized and reacted to form ferric hydroxide, two moles of hydrogen ion are produced. Thus, if ferrous iron is foam separated from acid drainage before oxidation, the subsequent neutralization will be less costly. Also, divalent ions are more effectively removed from solution by foaming than are trivalent or higher valent ions (13). Considering these facts, removal of iron from acid drainage as ferrous ion would be more efficient than oxidation and neutralization prior to foaming.

Experiments 45 and 46 were performed at temperatures between 1° and 8°C. The accumulation ratios for colloidal ferric hydroxide were 2.3 and 3 which is higher than in analogous experiments 42-44 conducted at 23° ± 2°. Foam fractionation works at low and ambient laboratory temperatures equally well.

(4) Foam Separation of Manganese and Iron from Acid Solution

Experiments 47-50 were designed to determine the efficiency of foam separation for removing manganese from acid solution (8). Experimental details are presented in Appendix C.

Several conclusions can be drawn from experiments 47-50. Manganese is accumulated in and removed from solution by the foam. Iron and manganese appear to be removed in proportion, iron at about 90% and manganese at about 50% under the experimental conditions. Thus, it would be expected that efforts to increase iron removal would result in an increase in manganese removal.

No significant difference in the removal of iron, calcium and manganese appears to result from the use of either Alipal EO-526 or Alipal CD-128. However, the use of Alipal EO-526, at a given concentration, results in less water removed with the foam.

pH in the range 3.3 - 5.6 has no apparent effect on iron and manganese removal and water loss. However, calcium is more completely removed at the lower pH values.

(5) Foam Separation of Iron, Calcium and Magnesium from Synthetic and Real Acid Mine Drainage

Eight foam separation experiments (Nos. 51 - 58) were conducted with synthetic and real acid mine drainage. The composition of synthetic acid mine water used in experiments 51-52 was:

0.997 g $FeSO_4 \cdot 7H_2O$)
0.344 g $CaSO_4 \cdot 2H_2O$)
0.186 g $Al_2(SO_4)_3 \cdot 18H_2O$)
0.246 g $MgSO_4 \cdot 7H_2O$
0.024 g $MnSO_4 \cdot H_2O$

Dissolved in one
liter of 0.01 N H_2SO_4

Similar compositions are common in actual acid mine drainage. Calculated for the three most concentrated metal ions, the liquid contained 200 ppm of ferrous iron, 80 ppm of calcium, and 24 ppm of magnesium. Its pH was 2.0.

The six experiments 53 - 58 were performed on actual mine water samples at the South Greensburg Discharge (FWQA No. 16-003) in western Pennsylvania on February 5, 1970. The details for experiments 51 - 58 are presented in Appendix D.

The few experiments performed on artificial and real acid mine drainage indicate that accumulation of iron, calcium and magnesium in foam is feasible in complex solutions. The production of persistent foams was greatly reduced in the complex solutions. The addition of gelatin (experiments 55 and 56) improved foam production and persistence. It is evident that further work is required with surfactants for increasing foam production in complex mixtures.

The sample of natural acid mine drainage was subjected to foaming within 24 hours of sampling. Before the foaming experiments were started, significant oxidation and precipitation of ferric hydroxide iron had occurred as evidenced by red precipitate in the sampling containers. Thus, the inconsistencies in duplicate experiments 57 and 58 are explained by colloidal iron and the well known scavenging properties of ferric hydroxide for other soluble metal ions.

The surfactants employed were selected for low cost, not selectively for particular ions. Consequently, when calcium, magnesium, aluminum and other metal ions are present, the surfactant is distributed among them. Hence, the ratio of surfactant to iron required to achieve a useful accumulation in the foam must be greater than when ferrous ions are the only multivalent cations in solution. Further research is required to clarify the inter-relationship between complex solutions, surfactant and foam production.

SECTION VI

ECONOMIC EVALUATION AND SUMMARY

The capital and operating costs for batch treatment of acid mine drainage can be estimated with the data from experiments 1 - 18. Table VI gives a material balance for removing the major metallic constituent, ferrous iron, at an effective rate of 0.1 mgd. The material balance was constructed from data obtained in the numerous batch experiments conducted to date. It represents a conservative estimate of the degree of foam separation obtainable under simple batch operation without surfactant recovery, regeneration and reuse, and without complete foam drainage.

If the concentration of surfactant is kept large enough to maintain a surfactant to iron ratio sufficient to provide complete reaction of iron and surfactant and equilibrium adsorption of surfactant to bubble surfaces within bubble residence times in the solution, then the rate of iron separation will be based on the volume rate of air passed through the solution. Greater than 99 per cent of the iron can be removed by keeping the surfactant to iron concentration ratio at 40 (as indicated by the data in Figures 6 and 8). In order to remove this quantity of iron, the residual surfactant concentration remains relatively high and a final suction foaming (see Figure 3) is required to reduce this concentration. As shown in Table VII, the chemical costs are significantly reduced by the final suction foaming assuming that the recovered surfactant can be reused. Thus, methods to recover, regenerate and reuse surfactant are required to reduce costs. The chemical cost estimate is based on a surfactant cost of 30 cents per pound and a NaOH cost of 5 cents per pound. These costs can probably be reduced by purchase of large quantities.

The material balance (Table VI) and the chemical cost estimate (Table VII) are calculated on 0.1 mgd, but can be scaled

TABLE VI

Material Balance for Batch Foam Separation of Iron

	Working Parameters$^{(1)}$	0.1 MGD Pilot-Plant Scale Initial Solution $^{(2)}$	0.1 MGD (2) Pilot Plant Scale Residual Solution	0.1 MGD (2) Pilot Plant Scale Suction Foaming
Water Volume, l	2.2	1.50×10^5	9.3×10^4	8.1×10^4
Fe, g	.576	4.50×10^4	500	--
Fe, ppm	277	300	5.4	--
Fe Removal Rates (3),				
- $g \cdot min^{-1}$	3.0×10^{-4}	8.34×10^{1}	--	--
- $g \cdot cm^{-3}$ air	8.34×10^{-7}	8.34×10^{-7}	--	--
Fe Removal, %	70	--	99	--
Surfactant, g	21.45	1.80×10^6	1.00×10^5-7.44×10^4	2.11×10^4
Surfactant, ppm	10,760	12,000	1080 - 800 (7)	260
Surfactant Removal Rates (4)				
initial - $g \cdot min^{-1}$	1.80×10^{-2}	3.87×10^6	--	--
initial - $g \cdot cm^{-3}$ air	5.00×10^{-5}	5.00×10^{-5}	--	--
average - $g \cdot cm^{-3}$ air	3.14×10^{-5}	3.14×10^{-5}	--	--
Surfactant Removal, %	89	--	94 - 96 (8)	98
Air Rate, $cm^3 \cdot sec^{-1}$	6	1.67×10^6	--	1.67×10^7
$\frac{\text{Air Volume}}{\text{Water Volume}}$	2.78×10^2	3.60×10^2 (5)	--	--
Drainage Time, sec	1100	1100 (6)	--	--

Table VI (continued)

	Working Parameters(1)	0.1 MGD Pilot-Plant Scale Initial Solution(2)	0.1 MGD(2) Pilot Plant Scale Residual Solution	0.1 MGD (2) Pilot Plant Scale Suction Foaming
Foaming Time, min	1695	540	--	70
$\frac{\text{Surfactant}}{\text{Fe}}$ Weight Ratio	40	40	--	--
Water Loss, %	38	--	38	46

(1) Based on Experiments 1 - 18.

(2) Based on Scale increase of Experiments 1 - 18.

(3) Fe removal rate held constant by holding $\frac{\text{Surfactant}}{\text{Fe}}$ ratio at 40; see Figure 8.

(4) Surfactant rate will decrease as surfactant concentration is decreased by foaming, see Figure 6.

(5) Air volume to water volume ratio increased to increase air-liquid surface area throughput and thus increase Fe removal.

(6) Pilot-scale foaming apparatus designed to maintain drainage time.

(7) 1080 ppm based on average surfactant removal rate; 800 ppm based on minimum surfactant concentration to sustain persistent foam (Figure 6).

(8) Surfactant removal increased due to increase in air:water volume ratio.

TABLE VII

Chemical Cost Estimate

Chemical costs are based on the material balance (Table VI) and the following conditions:

1.	Surfactant	$0.30\ \$\cdot lb^{-1}$
2.	NaOH	$0.05\ \$\cdot lb^{-1}$
3.	OH:Fe mole ratio equals 3 for surfactant regeneration	

	For Pilot-Plant Material Balance	Additional Suction Foaming for Reduction of Surfactant Loss
Water Volume, l	1.50×10^5	--
Fe Removal, g	4.45×10^4	--
NaOH used for surfactant regeneration, g	9.51×10^4	--
Surfactant Loss, g	1.00×10^5	2.11×10^4
NaOH Cost, $	10.50	10.50
Surfactant Cost, $	66.00	13.90
Total Chemical Cost, $	76.50	24.40
Total Chemical Cost per 1000 gal, $	1.93	.61

up linearly for 1.0 mgd. Consideration of process scale criteria required to maintain a workable system is expressed in the conceptual process plant design shown in Figure 9. Those process scale criteria include foam drainage time, residence time of a bubble in the liquid, foaming time, and the effective volume treatment rate. The process conceptually operates in a cylindrical foaming tank with a larger diameter cylindrical foam draining tank and drains while passing radially at a slight grade through the drainage section. The foam is collected at the circumference of the draining tank.

The near complete removal of iron and the reduction of surfactant by suction foaming is accompanied by considerable entrainment of water with the foam (low volume reduction factor = 2.2; see Figure 7). Since the volume reduction factor is proportional to drainage time, a means of increasing foam drainage is required.

An equipment cost estimate is given in Table VIII for effective process rates of 0.1 and 1.0 mgd based on the process schematic in Figure 10. Estimated power costs for both scales of batch treatment are given in Table IX. Power costs are based on a rate of 2.8 cents per kilowatt-hour and would be high for many areas.

Using the delivered equipment costs, the total capital costs for both 0.1 and 1.0 mgd batch foam separation plants are estimated (Tables X and XI).

In summary, the operating costs for 0.1 and 1.0 mgd foam separation are estimated in the range of 0.71 - 2.16 $·1000 gal^{-1} under the conditions stipulated in the estimates and in exclusion of personnel salaries. The capital cost estimates for complete plants range \$4.13 - 6.46 x 10^5 and \$1.53 - 1.7 x 10^6 for 0.1 mgd and 1.0 mgd capacities, respectively. It is estimated that the cost per unit volume of treatment can be reduced by continuous flow in contrast with batch operation. The basic equipment costs and thus the capital costs are possibly over estimated for continuous flow operation since the capacity of the

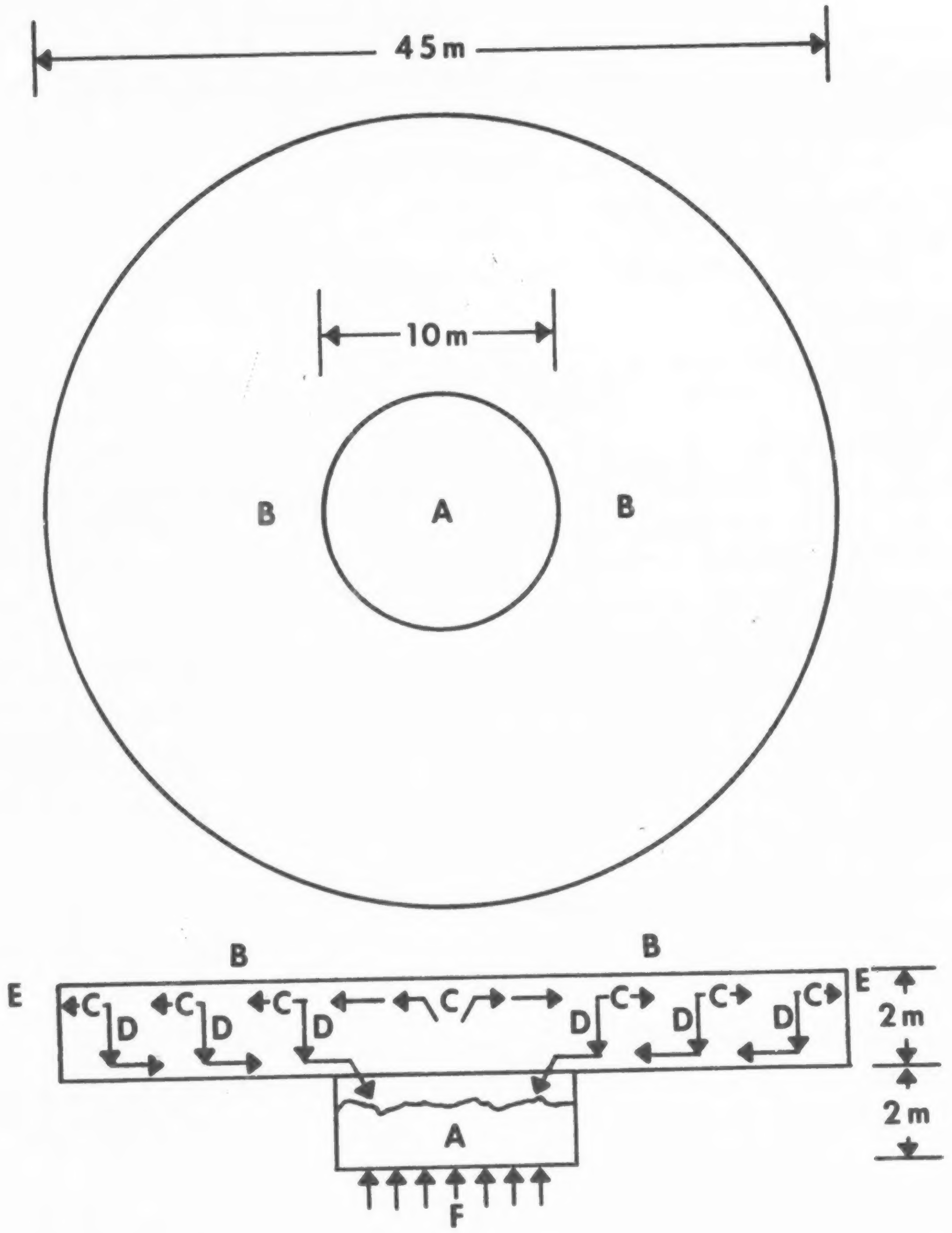
45m
10m
B
A
B
B
B
E
C
D
C
D
C
D
C
D
C
D
C
D
C
E
2m
2m
A
F

FIGURE 9

CONCEPTUAL DESIGN OF A FEASIBLE FOAM SEPARATION PLANT FOR BATCH TREATMEMT OF ACID MINE WATER. (DIMENSIONS SHOWN ARE FOR AN EFFECTIVE TREATMENT OF 0.1 MGD.)

LEGEND

A	Foaming tank	D	Foam drainage path
B	Foam drainage tank	E	Foam exit
C	Foam flow path	F	Air

TABLE VIII

Estimate of Delivered Equipment Costs

(ENR Index 1308)

	0.1 MGD	1.0 MGD
Feed Pump, Centrifical,		
50 ft head, 100-2000 $gal \cdot min^{-1}$, 30-50 hp motor	\$ 1,600 - 2,175	
50 ft head, 6.25 x 10^3 $gal \cdot min^{-1}$, 3 - 2000 $gal \cdot min^{-1}$ pumps, 50 hp motors each		\$ 6,000 - 7,000
Air Compressors,		
3.33 x 10^3 $ft^3 \cdot min^{-1}$, reciprocating, 34 hp	37,500 -81,000	
3.33 x 10^4 $ft^3 \cdot min^{-1}$, centrifical turbine, 300 hp		250,000-280,000
Surfactant Pump,		
Rotary 100-500 $gal \cdot min^{-1}$	1,060 - 2,380	
Centrifical 1000-2000 $gal \cdot min^{-1}$		1,600 - 2,175
Foaming Tank, Cast iron,		
37,500 gal	11,000 -12,500	
375,000 gal		35,000 -37,500
Foam Draining Tank, Cast iron,		
460,000 gal	50,000 -62,500	
4,600,000 gal		125,000-140,000
Surfactant Regeneration Tank,		
20,000 gal	8,100 -10,000	
200,000 gal		12,500 -15,000
Surfactant Storage Tank,		
2,000 gal	2,250 0 2,500	
20,000 gal		8,100 -10,000
	\$111,510-173,055	\$438,200-491,675

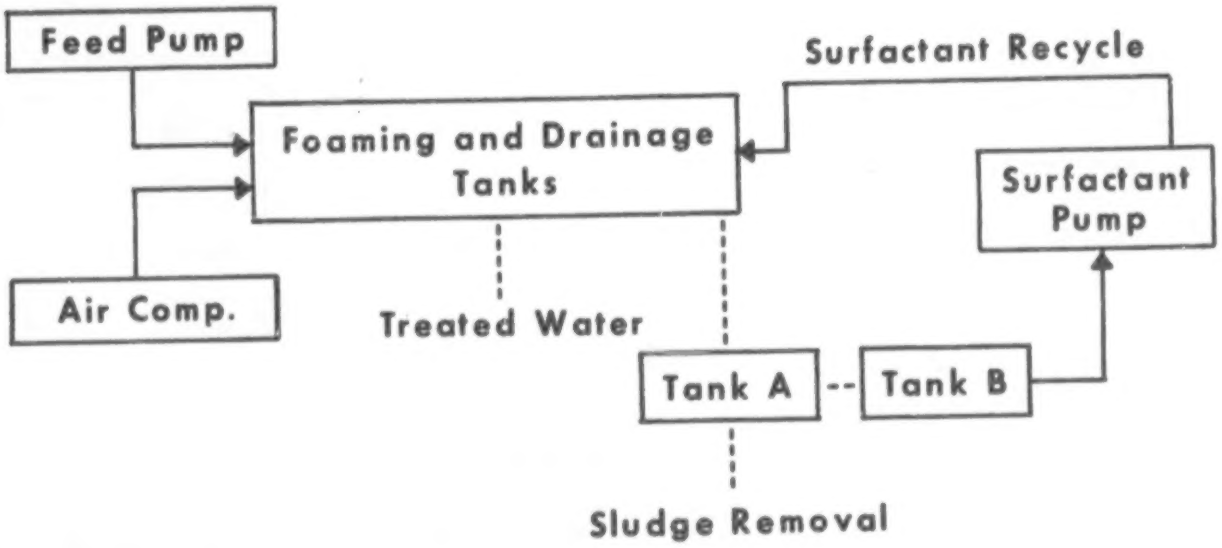
Feed Pump
Surfactant Recycle
Foaming and Drainage Tanks
Surfactant Pump
Air Comp.
Treated Water
Tank A
Tank B
Sludge Removal

FIGURE 10

SCHEMATIC DIAGRAM FOR BATCH FOAM FRACTIONATION REMOVAL OF IRON

TANK A	Surfactant regenerator and thickening.
TANK B	Fresh surfactant storage.
----------	Gravity flow.

TABLE IX

Estimation of Power Costs for Process Equipment at $0.028\$\cdot\mathrm{KWH}^{-1}$

0.1 MGD

	$\$\cdot\mathrm{hr}^{-1}$	Time per Batch hr	Cost per Batch $\$$	Cost per 1000 gal, $\$$
Feed Pump, 50 hp	1.05	.312	.328	.009
Air Compressor	0.71	9	6.390	.170
Surfactant pump	0.21	9	1.890	.050
			8.608	.229

1.0 MGD

	$\$\cdot\mathrm{hr}^{-1}$	Time per Batch hr	Cost per Batch $\$$	Cost per 1000 gal, $\$$
Feed Pumps, 3-50 hp	3.15	1.00	3.15	.009
Air Compressor	6.26	9.00	56.50	.150
Surfactant Pump	1.05	9.00	9.45	.025
			69.10	.184

TABLE X

Capital Costs Estimate - 0.1 MGD

(Accuracy Averages + 15 to -30 Percent (15))

1.	Delivered equipment costs from references and on current index basis		$111,510 - 173,055
2.	Installed equipment costs Item 1 x 1.43		159,459 - 247,468
3.	Process piping		23,918 - 37,120
	Type plant	Per cent of item 2	
	Solid-fluid	15	
4.	Instrumentation		11,162 - 17,322
	Amount of automatic control	Per cent of item 2	
	Some	7	
5.	Buildings and site development		31,891 - 49,493
	Type of plant	Per cent of item 2	
	Outdoor	2	
6.	Auxiliaries		0
	Extent	Per cent of item 2	
	Existing	2	
7.	Outside lines		4,783 - 7,424
	Average length	Per cent of item 2	
	Short	3	
8.	Total physical plant costs Sum of items 2 + 3 + 4 + 5 + 6 + 7 = subtotal		231,213 - 358,827
9.	Engineering and construction		80,924 - 125,589
	Complexity	Per cent of item 8	
	Simple	35	
10.	Contingencies		57,803 - 89,706
	Type process	Per cent of item 8	
	Subject to change	25	
11.	Size factor		42,646 - 71,765
	Size Plant	Per cent of item 8	
	Experimental unit (< $5,000)	20	
12.	Total plant or fixed capital costs: Sums of items 8 + 9 + 10 + 11 = total		$412,586 - 645,887

TABLE XI

Capital Costs Estimate - 1.0 MGD

(Accuracy Averages +15 to -30 Percent (15))

1.	Delivered equipment costs from references and on current index basis.....................		$ 438,200	-	491,675
2.	Installed equipment costs......................		626,626	-	703,095
	Item 1 x 1.43				
3.	Process piping.................................		93,993	-	105,464
	Type plant	Per cent of item 2			
	Solid-fluid.................	15			
4.	Instrumentation.................................		43,863	-	49,216
	Amount of automatic control	Per cent of item 2			
	Some.........................	7			
5.	Buildings and site development.................		125,325	-	140,619
	Type of plant	Per cent of item 2			
	Outdoor.....................	20			
6.	Auxiliaries.....................................		0		
	Extent	Per cent of item 2			
	Existing....................	0			
7.	Outside lines...................................		18,798	-	21,092
	Average length	Per cent of item 2			
	Short.......................	3			
8.	Total physical plant costs				
	Sum of items 2 + 3 + 4 + 5 + 6 + 7 = subtotal		908,605	-	1,019,486
9.	Engineering and construction...................		299,839	-	336,430
	Complexity	Per cent of item 8			
	Simple......................	33			
10.	Contingencies..................................		227,151	-	254,871
	Type process	Per cent of item 8			
	Subject to change...........	25			
11.	Size factor....................................		90,860	-	101,948
	Size Plant	Per cent of item 8			
	Small commercial plant ($0.5-2 x 10)...............	10			
12.	Total plant or fixed capital costs				
	Sums of items 8 + 9 + 10 + 11 = total........		$1,526,455	-	1,712,735

feed pumps could be significantly reduced. The tanks and air compressors would remain of the same capacities. The key to reducing operating costs is reuse of surfactant.

The specific conclusions reached and recommendation extended as a result of this research are listed in Sections I and II, respectively.

In general, the feasibility of foam fractionation for treatment of acid mine drainage has been established. However, two areas are in need of further research. Methods to promote more rapid and complete foam drainage and methods to increase surfactant recovery, regeneration and reuse are required.

Surfactant type and the design of foam drainage chambers are two important controls of foam drainage in need of further investigation. With development of efficient methods for surfactant reuse, the costs of foam separation could be significantly reduced. In addition, with more efficient economic use of surfactant, the use of a wider range of surfactants without as rigid cost restraints could be investigated.

Our work to date and that of others (16)(17)(18)(19) suggest that continuous foam fractionation has great potential for improving the removal of metal ions from mine drainage. Virtually any full-scale foam separation would be most efficiently conducted on a continuous flow basis. The results of batch experiments should be extended to continuous flow operation.

SECTION VII

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SECTION VIII

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SECTION IX

APPENDICES

Appendix A. Experimental Detail: Foam Separation of Iron and Calcium from Partially Neutralized Solutions, Experiments 19-33.

In many of the following experiments, the duration of foam drainage is marked for every foam; e.g., (10 g; 1100 sec) means that 10 g of wet foam were collected (after correction for evaporation) at a foaming rate such that the drainage lasted 1100 seconds.

Experiment 19

This experiment was similar to no. 18 in that foaming was extended until the surfactant concentration in the residual solution was greatly reduced. However, the initial solution contained calcium chloride and manganese sulfate instead of sulfuric acid. Its composition was 2.2 g Alipal EO-526, 2 millimoles calcium chloride, 2.27 mg ferrous chloride, and 11 mg $MnSO_4 \cdot H_2O$ in 2245 cm^3 of aqueous solution. Thus, the weight concentrations were 980 ppm Alipal EO-526 solution (or about 590 ppm solid surfactant), 36 ppm calcium, 4.5 ppm iron, and 1.5 ppm manganese.

The solution was foamed with compressed air in a foam tower of 7.0 cm^2 cross-section and 49 cm height. Consequently, the rate V of foaming (cm$^3 \cdot$sec^{-1}) corresponded to a drainage time equal to $t = 343/V$ sec. The volume rate V was changed from time to time as indicated in the results.

The first residual solution, whose composition is shown in the 10th line of the table, was foamed in a beaker, as illustrated in Figure 3. The 11th line indicates the composition of the foam thus obtained, and the 12th, the composition of the second residual solution.

Experiment 19 (continued)

Analytical Results:

	Foaming Time, min	Foam Collected g	Drainage Time, sec	Surfactant ppm	Calcium ppm	Iron ppm
Initial Solution	-	-	-	1100 (980)	34 (36)	5.0 (4.5)
First Foam	120	75	490	2760	110	7.2
Second Foam	780	18	1040	19800	400	16.7
Third Foam	120	66	515	3430	83	10.5
Fourth Foam	240	268	294	2030	66	11.1
Fifth Foam	180	51	295	4650(?)	87	10.6
Sixth Foam	60	27	206	2670	50	?
Seventh Foam	60	57	50 - 100	1090	50	10.5
Eighth Foam	Several	59	25	730	46	2.0
Residual Solution	-	-	-	250	20	0.7
Beaker Foam	15	175	-	255	21	3.2
Second Residual Solution	-	-	-	75	20	1.4

Test Results:

	Surfactant Removal	Ca Removal	Fe Removal	Water Loss with Foam
First 8 Foams	83%	57%	90%	28%
Beaker Foam	95%	62%	82%	35%

Experiment 20

This experiment was analogous to experiment 19, except that Alipal CD-128 was used instead of Alipal EO-526. Alipal CD-128, if otherwise suitable, would be preferable to Alipal EO-526 as CD-128 is biodegradable. The pH of the initial solution was 3.4. See Analytical and Test Results on page 58.

Experiment 21

Two grams of sodium dodecyl sulfate + 3.5 cm^3 of 0.1 M $FeSO_4$ were added to 2 liters of saturated gypsum solution. The initial pH was 5.8. As no foam could be produced at lower rates, the rate of air injection was maintained between 2.8 and 3.6 cm$^3\cdot$sec^{-1} in a 42 cm tall foam tower with a cross section of 23 cm^2. Thus the drainage time varied between 340 and 270 seconds.

Analytical Results:

	Surfactant	Iron	Calcium
Initial Solution	980 ppm	9.24 ppm (theor.9.8)	618 ppm
Residual Solution	516	8.50	228
Foam (33 g)	17600	33.4	500

Test Results:

	Surfactant Removal	Ca Removal	Fe Removal	Water Loss with Foam
1 Foam	48%	64%	9.5%	1.6%
Accumulation Ratio	18	0.8	3.6	-

Experiment 20 (continued)

Analytical Results:

	Foaming Time min	Foam Collected g	Drainage Time, sec	Surfactant ppm	Calcium ppm	Iron ppm
Initial Solution	-	-	-	950 (980)	34.4 (36)	4.9 (4.5)
First Foam	750	16	1030	9800	470	114
Second Foam	270	82	490	4500	114	24
Third Foam	240	296	298	1830	46	2.3
Fourth Foam	60	171	211	1560	47	1.4
Fifth Foam	7	194	49	1110	32	1.4
Sixth Foam	2	127	27	945	29	1.5
Residual Solution	-	-	-	800(?)	19	0.8

Test Results:

	Surfactant Removal	Ca Removal	Fe Removal	Water Loss with Foam
6 Foams	49%	67%	90%	39%

Experiment 22

Two grams of sodium dodecyl sulfate + 3.5 cm^3 of 0.1 M $FeSO_4$ in 10 cm^3 of saturated gypsum solution were added to 1900 cm^3 of water. The initial pH was 4.4.

Analytical Results:

	Surfactant	Iron	Calcium
Initial Solution	980 ppm	9.4 ppm	3.2 ppm
Residual Solution	450	0.06	0.8
First Foam (10 g; 1100 sec)	13000	163	114
Second Foam (118 g; 300 sec)	6200	62	89
Third Foam (113 g; 225 sec)	3200	18	2.3

Test Results:

	Surfactant Removal	Ca Removal	Fe Removal	Water Loss with Foam
3 Foams	62%	79%	99%	18%
Accumulation Ratio	13, 6, 3	36, 28, 0.7	17, 7, 2	-

Experiment 23

Two grams of sodium dodecyl sulfate + 35 cm^3 of 0.1 M $FeSO_4$ in 100 cm^3 of saturated gypsum solution were added to 1900 cm^3 of water. The initial pH was 2.95.

Analytical Results:

	Surfactant	Calcium
Initial Solution	980 ppm	32 ppm
Residual Solution	390	24
First Foam (13 g; 925 sec)	8200	142
Second Foam (180 g; 160-107 sec)	6200	180
Third Foam (117 g; 100 sec or less)	4300	53

Experiment 23 (continued)

Test Results:

	Surfactant Removal	Ca Removal	Water Loss with Foam
3 Foams	66%	36%	15%
Accumulation Ratio	8.3, 6.2, 4.3	4.4, 5.7, 1.7	-

Experiment 24

Two grams of sodium dodecyl sulfate + 100 cm^3 of 0.1 M $FeSO_4$ in 500 cm^3 of saturated gypsum solution were added to 1400 cm^3 of water. The initial pH was 2.45.

Analytical Results:

	Surfactant	Calcium
Initial Solution	980 ppm	270 ppm
Residual Solution	180	230
First Foam (41 g; 1200 sec)	5300	590
Second Foam (260 g; 140-60 sec)	4100	310

Test Results:

	Surfactant Removal	Ca Removal	Water Loss with Foam
2 Foams	84%	28%	15%
Accumulation Ratio	4.5, 4.2	2.2, 1.2	-

Experiment 25

Two grams of sodium dodecyl sulfate + 35 cm^3 of M $FeSO_4$ were combined in 2 liters of saturated gypsum solution. The initial pH was 2.40.

Analytical Results:

	Surfactant	Iron	Calcium
Initial Solution	1100 ppm	920 ppm	618 ppm (theor.)
Residual Solution	460	1030	?
First Foam (12 g; 140 sec)	28000	16500	1100
Second Foam (27 g; 115-82 sec)	6600	9400	270

Test Results:

	Surfactant Removal	Ca Removal	Fe Removal	Water Loss with Foam
2 Foams	59%	-	0%	1.9%
Accumulation Ratio	26, 6	2, 0.4	18, 10	-

Experiment 26

Eight grams of sodium dodecyl sulfate + 35 cm^3 of 0.1 M $FeSO_4$ in 100 cm^3 of saturated gypsum solution were combined with 1900 cm^3 of water. The initial pH was 3.2.

Analytical Results:

	Surfactant	Iron	Calcium
Initial Solution	3820 ppm	80 ppm(theor. 98)	32 ppm
Residual Solution	1760	50	?
First Foam (98 g; 1200 sec)	6600	1120	63
Second Foam (139 g; 1200 sec)	11500	3300	153
Third Foam (183 g; 1200 sec)	17000	2900	134

Experiment 26 (continued)

Test Results:

	Surfactant Removal	Ca Removal	Fe Removal	Water Loss with Foam
3 Foams	63%	-	50%	21%
Accumulation Ratio	1.7, 3.0, 4.4	2, 5, 4	14, 41, 36	-

Experiment 27

Eight grams of sodium dodecyl sulfate + 100 cm^3 of 0.1 M $FeSO_4$ in 500 cm^3 of saturated gypsum solution were added to 1500 cm^3 of water. The initial pH was 2.85.

Analytical Results:

	Surfactant	Iron	Calcium
Initial Solution	4000 ppm	300 ppm(theor. 275)	128 ppm
Residual Solution	3130	?	128
First Foam (35 g; 960 sec)	12000	400	290
Second Foam (280 g; 960-40 sec)	10400	320	50 (?)

Test Results:

	Surfactant Removal	Ca Removal	Fe Removal	Water Loss with Foam
2 Foams	33%	15%	-	15%
Accumulation Ratio	3, 2.6	2.3, 0.4	1.3, 1.1	-

Experiment 28

Eight grams of Alipal CD-128 + 35 cm^3 of 0.1 $\underline{M}$ $FeSO_4$ in 100 cm^3 of saturated gypsum solution were combined with 1900 cm^3 of water. The initial pH was 2.9.

Analytical Results:

	Surfactant	Iron	Calcium
Initial Solution	4000 ppm (theor.)	98 ppm (theor.)	30.4 ppm (theor. 29.5)
Residual Solution	3300	39	14.4
First Foam (39 g; 1100 sec)	13000	210	81
Second Foam (30 g; 1100 sec)	28200	430	157
Third Foam (58 g; variable)	52200	1220	706

Test Results:

	Surfactant Removal	Ca Removal	Fe Removal	Water Loss with Foam
3 Foams	23%	56%	63%	6.2%
Accumulation Ratio	5.2, 7.0, 13	2.6, 5.2, 23	2.2, 4.4, 12	-

Experiment 29

Two grams of Alipal CD-128 + 3.5 cm^3 of 0.1 $\underline{M}$ $FeSO_4$ were combined with 2 liters of saturated gypsum solution. The initial pH was 4.15.

Analytical Results:

	Surfactant	Iron	Calcium
Initial Solution	1000 ppm(theor.1000)	7.2 ppm	800 ppm(theor.618)
Residual Solution	420	6	944
First Foam (58 g; 250-220 sec)	3500	9.5	1100
Second Foam (227 g; 220-250 sec)	2500	9	710
Third Foam (88 g; 120→70→50 sec)	4100	10	1050

Experiment 29 (continued)

Test Results:

	Surfactant Removal	Ca Removal	Fe Removal	Water Loss with Foam
3 Foams	66%	0	32%	19%
Accumulation Ratio	3.5, 2.5, 4.1	1.4, 0.9, 1.2	1.3, 1.2, 1.4	-

Experiment 30

Alipal CD-128 2.05 g + 100 cm^3 of 0.1 M $FeSO_4$ in 500 cm^3 of saturated gypsum solution were combined with 1400 cm^3 of water.

Analytical Results:

	Surfactant	Iron	Calcium
Initial Solution	1100 ppm(theor.1025)	240 ppm	150 ppm (theor.)
Residual Solution	650	210	164
First Foam (62 g; 350→210 sec)	4000	240	190
Second Foam (227 g; 126 sec)	3500	130	42

Test Results:

	Surfactant Removal	Ca Removal	Fe Removal	Water Loss with Foam
2 Foams	49%	6.3%	25%	14%
Accumulation Ratio	3.7, 3.2	1.3, 0.3	1.0, 0.6	-

Experiment 31

Alipal CD-128 8.03 g + 100 cm^3 of 0.1 M $FeSO_4$ in 500 cm^3 of saturated gypsum solution were added to 1400 cm^3 of water.

Analytical Results:

	Surfactant	Iron	Calcium
Initial Solution	3900 ppm(theor. 4015)	230 ppm (theor. 275)	200 ppm (theor. 150)
Residual Solution	2640	285	152
First Foam (14 g; 1000 sec)	18900	230	520
Second Foam (37 g; 1000 sec)	9500	420	280
Third Foam (116 g; 1000 sec)	13800	100	300

Test Results:

	Surfactant Removal	Ca Removal	Fe Removal	Water Loss with Foam
3 Foams	38%	30%	0	8.3%
Accumulation Ratio	4.8, 2.4, 3.8	3.5, 1.9, 2.0	1.0, 1.8, 0.4	-

Experiment 32

Two grams of Alipal CD-128 + 35 cm^3 of M $FeSO_4$ were added to 2 liters of saturated gypsum solution. The initial pH was 2.4.

Analytical Results:

	Surfactant	Iron
Initial Solution	1060 ppm (theor.1000)	840 ppm (theor. 980)
Residual Solution	750	890
First Foam (17 g: 740 sec)	8900	-
Second Foam (79 g; 740→530 sec)	4800	830

Experiment 32 (continued)

Test Results:

	Surfactant Removal	Fe Removal	Water Loss with Foam
2 Foams	33%	0	4.7%
Accumulation Ratio	8.3, 4.5	1.0	-

Analytical data for calcium is absent because titration with EDTA and calcium was unsuccessful when the iron concentration was comparable to that of calcium. Attempts to sequester iron by adding an excess of potassium cyanide or to precipitate ferric hydroxide with hydrogen peroxide and ammonia followed by titration of the supernatant liquid were unsuccessful. When the oxalate method was adopted, not sufficient sample remained for analysis.

Experiment 33

Two grams of sodium dodecyl sulfate + 35 cm^3 of 0.1 M $FeSO_4$ in 100 cm^3 of saturated gypsum solution were combined with 1900 cm^3 of water.

Analytical Results:

	Surfactant	Iron	Calcium
Initial Solution	940 ppm(theor.980)	84 ppm (theor. 93)	32 ppm(theor.30)
Residual Solution	140	63	16
First Foam (20 g: 290 sec)	16500	340	440
Second Foam (235 g; 160→60 sec)	4400	?	71

Test Results:

	Surfactant Removal	Ca Removal	Fe Removal	Water Loss with Foam
2 Foams	87%	56%	34%	12%
Accumulation Ratio	17, 4.7	14, 2.2	4	-

Appendix B. Experimental Detail: Foam Separation of Iron and Calcium after Limestone Neutralization, Experiments 34 - 46.

Experiment 34

In this experiment 50 cm^3 of 0.1 M H_2SO_4 and 50 cm^3 of 0.1 M $FeSO_4$ were diluted with 900 cm^3 of distilled water in a 3-neck flask. One g of commercial sodium dodecyl sulfate (containing about 0.45 g of the active surfactant) was introduced. The pH of the initial solution was 3.0. Ten pellets of chemically pure calcium carbonate (0.07 g each) were sequentially added to the flask. Foam production from CO_2 evolution was negligible, but the pH was raised to 5.0. With the introduction of air through a dispersion tube, the lowest air rate at which (in the foam tower used) a foam could be collected was 4 $cm^3 \cdot sec^{-1}$ (corresponding to a drainage time of approximately 250 sec). With drainage times varying between 250 and 160 sec, 167 g of wet foam were collected in 3 hours. The concentration of iron in this foam was 170 $mg \cdot kg^{-1}$ as compared to 279 $mg \cdot kg^{-1}$ in the initial solution and 112 $mg \cdot kg^{-1}$ in the residual solution. Apparently ferric hydroxide formed in the flask was not concentrated in the foam. The aliquot withdrawn from the residual solution contained less ferric hydroxide precipitate than the part not analyzed. The concentration of calcium in the foam was 420 $mg \cdot kg^{-1}$. The amount of calcium needed for neutralizing 50 cm^3 of 0.1 M H_2SO_4 is 200 mg. Thus, some calcium was accumulated in the foam. It is not known, however, whether calcium carbonate powder was entrained with the foam and analyzed together with soluble calcium. The concentration of calcium in the residual solution was 480 $mg \cdot kg^{-1}$; presumably, some solid calcium carbonate was determined again.

Test Results:

67% removal of iron and 17% water loss with foam.

Experiment 35

To obtain a more copious evolution of foam, more concentrated solutions were used. 175 cm^3 of 0.1 M H_2SO_4, 175 cm^3 of 0.1 M $FeSO_4$ and 1 g of technical sodium dodecyl sulfate were diluted with 650 cm^3 of water. The initial concentration of iron was 980 mg·kg^{-1}. Ten calcium carbonate tablets (0.35 g each) were added to the solution. Foam formation by CO_2 evolution was negligible. The flask was left 16 hours during which precipitation of ferric hydroxide occurred. An aliquot of the supernatant solution contained 370 mg·kg^{-1} of iron, meaning that the precipitation was incomplete and that colloidal ferric hydroxide was presumably still present. The supernatant solution also contained 110 mg·kg^{-1} surfactant. Apparently the major part of the surfactant was adsorbed by the precipitate.

The liquid and precipitate were foamed, but negligible foam could be collected even at an air rate of 20 cm^3·sec^{-1} (corresponding to a drainage time of 50 sec). An aliquot of the supernatant solution contained 31 mg·kg^{-1} of iron and 69 mg·kg^{-1} of surfactant. Ferric hydroxide precipitation was more complete after aging.

The first supernatant solution contained 1400 mg·kg^{-1} of calcium. As the concentration sufficient to neutralize 175 cm^3 of 0.1 M H_2SO_4 in one liter is 700 mg·kg^{-1}, some calcium carbonate powder must have been suspended in the solution. The second supernatant solution contained 650 mg·mg^{-1}. This again shows that the separation between precipitate and solution was more complete after aging.

Test Results:

No foam produced.

Experiment 36

Because of the difficulties caused by the presence of suspended matter, the design of the tests was altered. Instead of adding calcium carbonate directly to the acid solution, the solution was filtered through a bed of calcium carbonate.

Thirty five grams of calcium carbonate powder were spread on a sintered glass filter and a solution of 100 cm³ 0.1 M H_2SO_4, 100 cm³ 0.1 M $FeSO_4$ and 1900 cm³ of water was filtered slowly through. The pH of the filtrate was 5.8 to 5.9. As the filtrate contained suspended ferric hydroxide, it was filtered through a filter paper. The iron content of the second filtrate was 20 $mg \cdot kg^{-1}$ as compared to an initial concentration before filtration of 266 $mg \cdot kg^{-1}$. The second filtrate was foamed with 2 g of technical sodium dodecyl sulfate. Foam was produced only at a high gas rate corresponding to a drainage time of 310 sec. Altogether, 157 g of foam was collected. The concentration of surfactant in it was 200 $mg \cdot kg^{-1}$. Apparently the main part of the surfactant was adsorbed by the precipitate. The iron concentration in the foam was 52 $mg \cdot kg^{-1}$ so that the accumulation ratio was 2.6. The surfactant concentration in the residual solution was 47 $mg \cdot kg^{-1}$, about 0.23 that in the foam, while the iron content was 15 $mg \cdot kg^{-1}$, about 0.29 that in the foam.

The residual solution was foamed in a beaker and 389 g of foam collected by suction through an inverted funnel. The concentration of surfactant in the foam was 92 $mg \cdot kg^{-1}$ (accumulation ratio of about 2) to 18 $mg \cdot kg^{-1}$ and the iron concentration lowered from 266 to 2 $mg \cdot kg^{-1}$.

Filtration through calcium carbonate naturally introduced calcium into the solution. Calcium in the first filtrate was 1800 $mg \cdot kg^{-1}$ which is much greater than would be produced (190 $mg \cdot kg^{-1}$) by neutralizing the sulfuric acid. In the second filtrate calcium was 180 $mg \cdot kg^{-1}$. Apparently, the second filtration removed the suspended calcium carbonate particles. In the first foam, 500 $mg \cdot kg^{-1}$ calcium was present (accumulation ratio was 2.8). The calcium concentration in the first and the second residual solutions was 400 and 470 $mg \cdot kg^{-1}$, respectively.

Test Results(foam separation):

	Surfactant Removal	Fe Removal	Water Loss with Foam
1 Foam	95%	31%	7.5%
Beaker Foam	99%	93%	20%
Accumulation Ratio	0.2, 2	2.6, 2.4	-

Experiment 37

A solution containing 100 cm^3 0.1 M H_2SO_4, 100 cm^3 0.1 M $FeSO_4$ and 1900 cm^3 water at a pH of 2.7 was filtered through 150 g of calcium carbonate powder placed in a layer approximately 4 cm thick. Since the filtrate contained ferric hydroxide, it was filtered again through an 8 cm thick calcium carbonate bed (300 g $CaCO_3$).

Two grams of sodium dodecyl sulfate were added to the second filtrate. The second filtrate contained 550 $mg \cdot kg^{-1}$ active surfactant, 58 $mg \cdot kg^{-1}$ iron and 640 $mg \cdot kg^{-1}$ calcium. The pH was 6.1. Thus, the major part of iron (208 out of 266 $mg \cdot kg^{-1}$) was removed by the reaction with calcium carbonate while some carbonate powder passed into the filtrate.

The second filtrate was foamed at a drainage time of 170 seconds. The concentrations in the 78 g of foam collected were 1625 $mg \cdot kg^{-1}$ calcium. Thus, the accumulation ratio for the surfactant was 3.0 and colloidal ferric hydroxide and calcium were not collected in the foam.

The first residual solution contained 219 mg·kg^{-1} surfactant, 2 mg·kg^{-1} iron, and 500 mg·kg^{-1} calcium. The solution was foamed and 406 g of wet foam were collected. The concentrations in the foam were 569 mg·kg^{-1} surfactant (accumulation ratio 2.6), 3 mg·kg^{-1} iron, and 580 mg·kg^{-1} calcium. The concentrations in the second residual solution were 58 mg.kg^{-1} surfactant, 2 mg·kg^{-1} iron, and 500 mg·kg^{-1} calcium. Thus, there was also practically no accumulation of either iron or calcium in the second foam.

Test Results:

	Surfactant Removal	Ca Removal	Fe Removal	Water Loss with Foam
2 Foams	92%	40%	95%	23%
Accumulation Ratio	3.0, 2.6	-	-	-

Experiment 38

A liquid consisting of 100 cm^3 0.1 $\underline{M}$ H_2SO_4, 100 cm^3 0.1 $\underline{M}$ $FeSO_4$ and 1900 cm^3 of water was filtered as in experiment 36. The filtrate was clear and had a pH of 6.0. After the addition of 2 g sodium dodecyl sulfate, it contained 570 mg·kg^{-1} active surfactant, 65 mg·kg^{-1} iron, and 680 mg·kg^{-1} calcium. Again, the major part of iron (201 out of 266 mg·kg^{-1}) was removed by reaction with $CaCO_3$ while greater amounts of calcium were introduced.

The filtrate was foamed at a drainage time of 130 seconds. Altogether 61 g of foam were collected. The concentrations in the residual solution were 345 mg·kg^{-1} surfactant, 66 mg·kg^{-1} iron, and 625 mg·kg^{-1} calcium.

Test Results:

No marked removal of either iron or calcium was achieved.

Experiment 39

A solution containing 100 cm^3 0.1 M $FeSO_4$, 100 cm^3 0.1 M H_2SO_4 and 1900 cm^3 water was filtered through 200 g of calcium carbonate spread on a porous glass plate in a layer about 5 cm thick. The pH of the filtrate was 6.1. The filtrate was foamed with 2 g of commercial sodium dodecyl sulfate containing about 45% of the active ingredient. The drainage time was 70 seconds because little foam was produced at a lower air rate.

Analytical Results:

	Surfactant	Iron	Calcium
Initial Solution	--	266 ppm (theor).	--
Filtrate	890 ppm	7	500 ppm
Foam (82 g)	7300	36	890
Residual Solution	300	5	450
Beaker Foam (188 g)	820	13	570
Second Residual Solution	170	3.4	320

Test Results:

	Surfactant Removal	Ca Removal	Fe Removal	Water Loss with Foam
1 Foam	68%	13%	31%	3.9%
Beaker Foam	83%	44%	58%	8.9%
Accumulation Ratio	8, 2.7	1.8, 1.3	5, 2.6	-

Experiment 40

A solution containing 100 cm^3 0.1 M $FeSO_4$, 100 cm^3 0.1 M H_2SO_4 and 1900 cm^3 water was filtered through 200 g of calcium carbonate spread on a porous glass plate in a layer about 5 cm thick. The pH of the filtrate was 6.1. Three grams of Alipal CD-128 were added, and the solution was foamed at drainage time of 1050 seconds.

Analytical Results:

	Surfactant	Iron	Calcium
Initial Solution	--	266 ppm (theor.)	--
Filtrate	1840 ppm	110	520 ppm
Foam (102 g)	9800	8	500
Residual Solution (no stirring)	1790	-	-
Residual Solution (after stirring)	1870	130	800

Test Results:

	Surfactant Removal	Ca Removal	Fe Removal	Water Loss with Foam
1 Foam	3.1%	0	0	4.8%
Accumulation Ratio	5	1	0.08	-

Experiment 41

Because colloidal ferric hydroxide could not be attached to the films of sodium dodecyl sulfate or Alipal CD-128 and because gelatin has been used to promote such attachments, an attempt was made to foam a filtrate of the type in experiments 36-40 after addition of 0.5 - 1 g gelatin. The initial pH was 6.6. As no stable foam was obtained, the pH was lowered to 4.5 and then to 2.5. Since foam persistence was not markedly improved by these changes, 0.177 g Alipal CD-128 was added to the solution which contained 1 g gelatin in 2 liters at pH 2.5. The drainage time was 700 seconds.

Analytical Results:

	Surfactant	Iron	Calcium
Initial Solution	--	266 ppm(theor.)	--
Filtrate	88 ppm (theor.)	90	450 ppm
Foam (295 g)	390	170	730
Foam (71 g)	490	130	730
Residual Solution	28	27	500

Test Results:

	Surfactant Removal	Ca Removal	Fe Removal	Water Loss with Foam
2 Foams	74%	8.2%	75%	17%
Accumulation Ratio	4.4, 5.6	1.6, 1.6	1.9, 1.4	--

Experiment 42

The initial solution was identical with those used before, containing 100 cm^3 0.1 $\underline{M}$ $FeSO_4$, 100 cm^3 0.1 $\underline{M}$ H_2SO_4, and 1900 cm^3 water. It was filtered through 150 g of calcium carbonate and 0.1 g Alipal CD-128 and 0.1 g gelatin was added to the filtrate. After these additions the pH was 4.4. The liquid was foamed first at a drainage time equal to 850 sec and then at 170 sec.

Analytical Results:

	Surfactant	Iron	Calcium
Initial Solution	--	236 ppm (theor.266)	--
Filtrate	59 ppm(calcd. 50)	110	250
Foam (49 g)	510	130	780
Foam (176 g)	140	90	580
Residual Solution	27	120	480

Test Results:

	Surfactant Removal	Ca Removal	Fe Removal	Water Loss with Foam
2 Foams	59%	0	2.6%	11%
Accumulation Ratio	9, 2.4	3, 2.3	1.1, 0.8	--

Experiment 43

This is a repetition of experiment 42. The pH of the filtrate after the addition of gelatin and Alipal CD-128 was 4.5. The duration of drainage is shown in the results.

Analytical Results:

	Surfactant	Iron	Calcium
Initial Solution	--	289 ppm(theor.266)	--
Filtrate	59 ppm(calcd.50)	150	560 ppm
Foam (39 g; 850 sec)	640	300	800
Foam (70 g; 750 sec)	340	60	720
Residual Solution	33	120	570

Test Results:

	Surfactant Removal	Ca Removal	Fe Removal	Water Loss with Foam
2 Foams	37%	3.5%	24%	5.2%
Accumulation Ratio	13, 7	1.4, 1.3	2,0.4	-

Experiment 44

This is a repetition of experiment 43 except that the pH of the filtrate was adjusted to 6.4 by adding 25 cm^3 of 0.1 M Na_2CO_3 solution.

Analytical Results:

	Surfactant	Iron	Calcium
Initial Solution	--	370 ppm(theor.266)	--
Filtrate	54 ppm(theor.50)	160	390 ppm
Foam (170 g; 850 sec)	220	100	540
Foam (85 g; 850 sec)	270	100	610
Residual Solution (stirred)	23	130	550

Experiment 44 (continued)

Test Results:

	Surfactant Removal	Ca Removal	Fe Removal	Water Loss with Foam
2 Foams	63%	0	28%	12%
Accumulation Ratio	4, 5	1.4, 1.6	0.6, 0.6	-

Experiment 45

Experiments 45 and 46 were similar to experiments 36 - 44, except that foaming was performed at low temperatures. The temperature of all previous experiments was 21°C - 25°C. Since the temperature of the acid mine drainage may be near 0°C, it was necessary to ascertain the feasibility of foam fractionation at reduced temperatures.

A solution of 100 cm^3 0.1 $\underline{M}$ $FeSO_4$, 100 cm^3 0.1 $\underline{M}$ H_2SO_4 and 1900 cm^3 water was filtered through 150 g of calcium carbonate spread on a fine grade sintered glass funnel. One gram gelatin and 0.1 g Alipal CD-128 were added to the filtrate. The pH was 6.6. The filtrate was kept between 2° and 8°C and subjected to foaming.

Analytical Results:

	Surfactant	Iron	Calcium
Initial Solution	--	277 ppm(theor.266)	--
Filtrate	57 ppm(theor.50)	120	540 ppm
Foam (78 g; 700 sec)	600	280	810
Residual Solution (stirred)	45	162	545

Test Results:

	Surfactant Removal	Ca Removal	Fe Removal	Water Loss with Foam
1 Foam	24%	2.8%	0	3.7%
Accumulation Ratio	10	1.5	2.3	0

Experiment 46

The preparation of the solution for foaming was identical to experiment 45. The pH of the solution was 6.6. The temperature of the solution was kept at 1° to 8°C and subjected to foaming.

Analytical Results:

	Surfactant	Iron	Calcium
Initial Solution	--	260 ppm(theor. 266)	--
Filtrate	58 ppm (theor. 50)	76	660 ppm
Foam (56 g; 800 sec)	1290	200	660
Residual Solution (stirred)	16	1.5	330

Test Results:

	Surfactant Removal	Ca Removal	Fe Removal	Water Loss with Foam
1 Foam	73%	51%	98%	2.7%
Accumulation Ratio	22	1.0	3	--

Appendix C. Foam Separation of Manganese and Iron from Acid Solution, Experiments 47 - 50

Experiment 47

A solution containing 1.1 g Alipal EO-526, 80.2 mg Ca, 10 mg Fe and 3.6 mg Mn in 2.25 l water was successively foamed at six increasing air rates. The initial solution pH was 5.5. The first residual solution was foamed in a beaker and 275 g wet foam was collected.

Analytical Results:

	Surfactant	Calcium	Iron	Manganese
Initial Solution	500 ppm	36 ppm	4.1 ppm	1.3 ppm
First Foam (61 g; 505 sec)	7800	157	9.5	2.25
Second Foam (30 g; 390 sec)	5400	128	9.1	1.4
Third Foam (23 g; 300 sec)	2960	102	10.8	4.0
Fourth Foam (34 g; 110 sec)	900	59	29.3	2.4
Fifth Foam (168 g; 27 sec)	310	38	14.5	1.3
Sixth Foam (48 g; 16 sec)	310	29	0.68	0.9
First Residual Solution	30	29	0.68	-
Beaker Foam (275 g)	80	30	0.68	1.6
Second Residual Solution	12	28	0.38	0.65

Test Results:

	Surfactant Removal	Ca Removal	Fe Removal	Mn Removal	Water Loss with Foam
First 6 Foams	95%	32%	86%	21%	16%
Beaker Foam	98%	44%	93%	63%	28%

Experiment 48

A solution containing 2.2 g Alipal EO-526, 80.2 mg Ca, 10 mg Fe and 3.6 mg Mn in 2.25 l water was successively foamed at eight increasing air rates. The initial solution pH was 3.3. The first residual solution was foamed in a beaker and 175 g wet foam was collected.

Analytical Results:

	Surfactant	Calcium	Iron	Manganese
Initial Solution	1120 ppm	34 ppm	5.0 ppm	--
First Foam (75 g; 490 sec)	2760	110	7.2	--
Second Foam (18 g; 1040 sec)	19800	400	16.7	--
Third Foam (66 g; 510 sec)	3430	83	10.5	5.2
Fourth Foam (268 g; 290 sec)	2030	66	11.0	2.7
Fifth Foam (51 g; 200 sec)	4650	87	10.6	0
Sixth Foam (27 g; 107 sec)	2760	50	--	4.2
Seventh Foam (60 g; 50 sec)	1090	50	10.5	3.1
Eighth Foam (59 g; 12 sec)	730	46	2.0	3.3
First Residual Solution	25	20	0.7	--
Beaker Foam (175 g)	255	21	3.2	--
Second Residual Solution	--	20	--	--

Test Results:

	Surfactant Removal	Ca Removal	Fe Removal	Mn Removal	Water Loss with Foam
First 8 Foams	98%	57%	90%	>46%	28%
Beaker Foam	298%	62%	>90%	>46%	35%

Experiment 49

A solution containing 1.1 g Alipal CD-128, 80.2 mg Ca, 10 mg Fe and 3.6 mg Mn in 2.25 l water was successively foamed at six increasing flow rates. The initial solution pH was 5.6. The first residual solution was foamed in a beaker and 525 g wet foam was collected.

Analytical Results:

	Surfactant	Calcium	Iron	Manganese
Initial Solution	560 ppm	34 ppm	3.4 ppm	1.4 ppm
First Foam (50 g; 520 sec)	5700	--	48	--
Second Foam (64 g; 280 sec)	1900	82	1.5	--
Third Foam (25 g; 200 sec)	1720	80	10	3.0
Fourth Foam (104 g; 98 sec)	660	47	0.8	1.6
Fifth Foam (79 g; 51 sec)	800	46	--	1.8
Sixth Foam (52 g; 27 sec)	710	49	0.4	0.9
First Residual Solution	190	26	0.4	0.9
Beaker Foam (525 g)	240	28	--	0.9
Second Residual Solution	235	24	0.31	0.9

Test Results:

	Surfactant Removal	Ca Removal	Fe Removal	Mn Removal	Water Loss with Foam
First 6 Foams	72%	36%	90%	45%	20%
Beaker Foam	75%	58%	95%	61%	40%

Experiment 50

A solution containing 2.2 g Alipal CD-128, 80.2 mg Ca, 10 mg Fe, and 3.6 mg Mn in 2.25 l water was successively foamed at six increasing air rates. The initial solution pH was 3.4.

Analytical Results:

	Surfactant	Calcium	Iron	Manganese
Initial Solution	955 ppm	34 ppm	4.9 ppm	2.0 ppm
First Foam (16 g; 1040 sec)	9800	460	114	12.2
Second Foam (82 g; 490 sec)	4500	114	24	4.1
Third Foam (296 g; 290 sec)	1830	46	2.3	1.6
Fourth Foam (171 g; 210 sec)	1560	47	1.4	1.8
Fifth Foam (194 g; 50 sec)	1120	32	1.4	1.5
Sixth Foam (127 g; 27 sec)	945	29	1.5	1.7

Test Results:

	Surfactant Removal	Ca Removal	Fe Removal	Mn Removal	Water Loss with Foam
First 6 Foams	78%	66%	90%	58%	39%

Appendix D. Foam Separation of Iron, Calcium and Magnesium from Synthetic and Real Acid Mine Drainage, Experiments 51 - 58.

Experiment 51

Two grams sodium dodecyl sulfate was added to 2 liters synthetic acid mine water, and the resulting liquid was foamed for a total of 6 hours.

Analytical Results:

	Surfactant	Iron	Calcium	Magnesium
Initial Solution	1240 ppm	122 ppm	83 ppm	19 ppm
Foam (66 g; 530→270 sec)	18600	215	250	30
Foam(71 g; 190→140 sec)	3760	160	110	25
Residual Solution	165	120	68	21

Test Results:

	Surfactant	Iron	Calcium	Magnesium
% Removal	88	8	24	0
Accumulation Ratio	15, 5.5	2, 1.3	3, 1.3	1.6, 1.3

Water Loss was 6.9%

Experiment 52

Repetition of Experiment 51.

Analytical Results:

	Surfactant	Iron	Calcium	Magnesium
Initial Solution	1370 ppm	115 ppm	88 ppm	40 ppm
Foam(158 g; 530→270 sec)	5600	95	140	50
Foam (246 g; 190→140 sec)	2600	110	88	40
Residual Solution	97	110	70	33

Test Results:

	Surfactant	Iron	Calcium	Magnesium
% Removal	94	24	36	34
Accumulation Ratio	4.1, 1.9	0.8, 1.0	1.5, 1.0	1.2, 1.0

Water Loss was 20%

Experiment 53

Two grams Alipal CD-128 were added to 2 liters natural acid mine water and the solution was foamed for 5.5 hours. The initial solution pH was 4.5.

Analytical Results:

	Surfactant	Iron	Calcium	Magnesium
Initial Solution	1270 ppm	90 ppm	220 ppm	85 ppm
Foam (34 g; 270→800 sec)	5500	105	240	100
Foam (19 g; 800 sec)	10200	110	310	160
Residual Solution	810	70	200	89

Test Results:

	Surfactant	Iron	Calcium	Magnesium
% Removal	38	22	9.1	0
Accumulation Ratio	4.3, 8.0	1.2, 1.2	1.1, 1.4	1.2, 1.9

Water Loss was 2.6%

Experiment 54

Two grams sodium dodecyl sulfate were added to 2 liters natural acid mine water and the solution was foamed for 5.5 hours. The initial solution pH was 4.5.

Analytical Results:

	Surfactant	Iron	Calcium	Magnesium
Initial Solution	1190 ppm	71 ppm	207 ppm	85 ppm
Foam (75 g; 360 sec)	16700	167	780	99
Foam (20 g; 360→180 sec)	10500	290	360	123
Residual Solution	56	79	160	73

Test Results:

	Surfactant	Iron	Calcium	Magnesium
% Removal	96	0	26	18
Accumulation Ratio	14, 8.8	2.3, 4.1	3.8, 1.7	1.2, 1.4

Water Loss was 4.7%

Experiment 55

One gram sodium dodecyl sulfate was added to 2 liters natural acid mine water. The initial solution pH was 4.5. Since the foam did not rise above the top of the tower, the foam present in the tower was washed into a receptacle and analyzed as the "first foam". To the residue, 1.0 g gelatin dissolved in 100 cm^3 natural acid mine water was added. The solution was foamed at drainage time of 510 seconds. The total foaming time was 6 hours.

Analytical Results:

	Surfactant	Iron	Calcium	Magnesium
Acid Mine Water	--	71 ppm	168 ppm	79 ppm
Initial Solution	540 ppm	79	171	117
First Foam (34 g)	19300	315	700	163
Second Foam (454 g)	385	137	230	176
Residual Solution	2	62	158	107

Test Results:

	Surfactant	Iron	Calcium	Magnesium
% Removal	> 99	29	28	29
Accumulation Ratio	36, 0.7	4, 2	4.1, 1.3	1.4, 1.5

Water Loss was 24%

Experiment 56

One gram Alipal CD-128 was added to 2 liters natural acid mine water. Two foams were collected in 6 hours of foaming. When the foam ceased to reach the top of the tower, 1.0 gram gelatin dissolved in 100 cm^3 natural acid mine water was mixed with the residual solution and a third foam collected.

Analytical Results:

	Surfactant	Iron	Calcium	Magnesium
Initial Solution	590 ppm	55 ppm	171 ppm	82 ppm
Foam (55 g; 350→520 sec)	5800	240	260	108
Foam (62 g; 350→150 sec)	5400	270	260	111
Foam (130 g; 3000 sec)	1080	80	150	59
Residual Solution	360	65	159	89

Test Results:

	Surfactant	Iron	Calcium	Magnesium
% Removal	46	0	18	4.5
Accumulation Ratio	10, 9, 2	4, 5, 1.5	1.5, 1.5, 1.5	0.9, 1.3, 1.3

Water Loss was 12%.

Experiment 57

Two grams Alipal EO-526 were dissolved in 2 liters natural acid mine water. The liquid was foamed for a total of 14 hours in which three foam fractions were collected. Then the residual solution was transferred into a beaker and foamed. The foam was removed by suction (Figure 3).

Analytical Results:

	Surfactant	Iron	Calcium	Magnesium
Acid Mine Water	---	68 ppm	156 ppm	87 ppm
Initial Solution	1130 ppm	89	182	100
Foam (45 g; 400 sec)	7500	190	210	110
Foam (61 g; 400 sec)	11800	170	230	154
Foam (70 g; 400 sec)	8000	300	210	82
First Residual Solution	220	61	152	87
Beaker Foam	500	72	165	66
Second Residual Solution	110	57	149	83

Test Results:

	Surfactant	Iron	Calcium	Magnesium
% Removal:				
First 3 Foams	~80	~31	~17	~13
Beaker Foam	~90	~36	~18	~17
Accumulation Ratio	7, 10, 7;	2, 2, 3.4;	1.2, 1.2, 1.2;	1.1, 1.5, 0.8

Water Loss was 8.8% for the first three foams.

Experiment 58

Repetition of Experiment 57.

Analytical Results:

	Surfactant	Iron	Calcium	Magnesium
Initial Solution	1000 ppm	75 ppm	157 ppm	110 ppm
Foam (17 g; 900 sec)	34000	250	410	200
Foam (20 g; 900 sec)	24800	315	335	175
First Residual Solution	340	76	160	88
Beaker Foam	800	83	310	202
Second Residual Solution	260	81	153	105

Test Results:

	Surfactant	Iron	Calcium	Magnesium
% Removal				
First Two Foams	~66	<1	<1	~20
Beaker Foam	~74	<1	~2	~4
Accumulation Ratio	34, 25	4, 4	2.6, 2.1	1.8, 1.6

Water loss was 1.9% for the first two foams.

BIBLIOGRAPHIC:

Horizons Incorporated, Treatment of Acid Mine Drainage by Foam Separation, Final Report, FWQA Program No. 14010 DEE, Contract No. 14-12-496
August, 1970

ABSTRACT

Basic experiments were conducted to establish the feasibility of foam fractionation in the treatment of acid coal mine drainage for the removal of the metal ions iron, calcium, manganese and magnesium. The

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independent variables controlling foam separation of metal ions were determined to be the concentration ratio of surfactant to iron, the air volume throughput, the foam drainage time, the total dissolved salt content and the type of surfactant used.

The major part of iron, calcium, manganese and magnesium can be foam separated from acid solution by proper control of the independent variables. Reduction of residual surfactant concentration in the treated water and reduction of water entrained with the foam are two areas in need of further investigation.

Operating and capital costs are estimated for 0.1 and 1.0 MGD batch treatment plants.

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10 Author(s)
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27 Abstract

Basic experiments were conducted to establish the feasibility of foam fractionation in the treatment of acid coal mine drainage for the removal of the metal ions iron, calcium, manganese and magnesium. The independent variables controlling foam separation of metal ions were determined to be the concentration ratio of surfactant to iron, the air volume throughput, the foam drainage time, the total dissolved salt content and the type of surfactant used.

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Foam separation was tested on acid drainage, partially lime neutralized drainage and complete limestone neutralized drainage. Tests on model solutions indicate that treatment of raw acid drainage is most feasible at present.

Operating and capital costs are estimated for 0.1 and 1.0 MGD batch treatment plants.

Abstractor P. J. Hanson

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